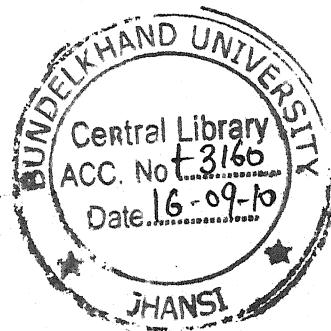


THE CATALYTIC ACTIVITY OF RUTHENIUM (III)  
IN META PERIODATE OXIDATION OF SOME  
ORGANIC COMPOUNDS, A KINETIC STUDY

A  
THESIS



Submitted to  
**Bundelkhand University, Jhansi**  
for the Award of the Degree of  
**DOCTOR OF PHILOSOPHY**  
IN  
**CHEMISTRY**  
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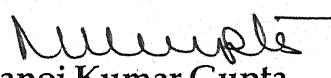


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# CERTIFICATE

Certified that the work embodied in this thesis entitled  
**"The catalytic activity of ruthenium (III) in metaperiodate  
oxidation of some organic compounds; a kinetic study"**  
is the result of original research carried out by **Mr. Shrish  
Chandra Tiwari** under my supervision and is suitable for  
submission for the award of Ph.D. Degree of Bundelkhand  
University, Jhansi

The thesis fulfil the required attendance as laid down  
by the university research organisation.

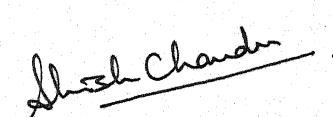
  
Manoj Kumar Gupta

## Declaration

I hereby declare that the thesis entitled  
**"The catalytic activity of ruthenium (III) in  
metaperiodate oxidation of some organic  
compounds; a kinetic study"** being submitted  
for the degree of Doctor of Philosophy to the  
Bundelkhand University, (U.P.) is an  
innovative piece of work carried out with  
utmost dedication by me and to the best to  
the my knowledge and belief it has not been  
submitted elsewhere.

Place : Jhansi

Date : 17 March, 2008

  
(Shrish Chandra Tiwari)

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Place : Jhansi

**Shrish Chandra Tiwari**

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## LIST OF ABBREVIATION

$\text{Os}^{\text{VIII}}$ or Osmium (VIII)	:	Osmium tetraoxide
$\text{Ru}^{\text{III}}$ or Ruthenium (III)	:	Ruthenium trichloride
K	:	Equilibrium constant
$K_{\text{obs}}$	:	Observed rate constant
$\Delta H^{\#}$	:	Enthalpy change for activation
$E_{\text{act}}^{\#}$	:	Energy of activation
$\Delta S^{\#}$	:	Entropy change for activation
$\Delta G^{\#}$	:	Gibbs free energy for activation
A	:	Arrhenius factor
FR	:	Fructose
GL	:	Glucose
GA	:	Galactose
MA	:	Maltose
LA	:	Lactose

## Preface

**Chapter- I** consists of a general idea of chemical kinetics, reaction rate, redox reactions osmium (VIII) and ruthenium (III) as catalysts, behavior of sodium metaperiodate as oxidant. A recent literature and relevant kinetics and mechanistic features have also been discussed.

**Chapter - II** explains methods involved in the preparation of solutions of reactants, method of determination of reaction rate and details of equations used in calculation of kinetic data.

**Chapter - III** includes the results of oxidation of some reducing sugars by  $\text{IO}_4^-$  in presence of ruthenium (III). The reducing sugars taken for the study are fructose, glucose, galactose, maltose and lactose.

**Chapter - IV** includes the study of oxidation of amino alcohols viz. 2- amino ethanol, 3-amino propanol, diethanolamine and triethanolamine by sodium metapriodate in presence of ruthenium (III) in acidic medium.

**Chapter - V** Includes the conclusion of kinetic result of the above mentioned compound of chapter III to IV.

The effect of several variation factors such as concentration of the ractants, pH, ionic strength and temperature etc. has been studied in each case. The mechanism of the oxidation has been proposed at the end of each chapter and relevant rate- laws have been derived and discussed.

# CONTENTS

<i>Particulars</i>	<i>Page No.</i>
<b>CHAPTER - 1</b>	
I. General Introduction	02
Platinum group metal-ions Catalysis	04
Ruthenium (III) as Catalyst	05
Osmium (VIII) as Catalyst	06
Metaperiodate as Oxidant	07
Effect of pH	11
Metaperiodate Oxidation	12
Reference	15
<b>CHAPTER - II</b>	
II Experimental	
Preparation of solutions	31
Experimental Method	32
Determination of the Order of Reaction	33
References	35
<b>CHAPTER - III</b>	
III Oxidation of Reducing Sugars by $\text{IO}_4^-$ in presence of Ruthenium (III)	
A. Introduction	37
B. Stoichiometry and Identification of Products ...	39
C. Effect of $\text{IO}_4^-$ on the Rate of Oxidation	41
D. Effect of [Substrate] on the Rate of Oxidation	47
E. Effect of [Alkali] on the Rate of Oxidation	55
F. Effect of $[\text{RuCl}_3]$ on the Rate of Oxidation	65
G. Effect of Temperature of the Rate of Oxidation	75

H. Influence of Ionic Strength	85
I. Evidence for Complex Formation	91
J. Kinetic Results at a Glance	93
K. Reacting Species	97
L. Mechanism for Oxidation Process	101
M. Derivation of Rate Law	102
N. Rate Law and Experimental Results	104
O. References	105
<b>Appendix</b>	115
<b>CHAPTER - IV</b>	
<b>IV. Oxidation of amino alcohols by <math>\text{IO}_4^-</math> is presence of Ruthenium (III).</b>	
A. Introduction	147
B. Stoichiometry	149
C. Effect of Variation in Sodium meta periodate concentrations	151
D. Effect of Variation in aminoalcohols concentrations	160
E. Effect of Variation in Ruthenium (III) concentrations	160
F. Effect of Variation in Perchloricacid concentrations	168
G. Influence of Neutral Salt	185
H. Effect of $\text{Cl}^-$ on the rate of reaction	185
I. Effect of Variation in temperation	188
J. Discussion	191
K. References	198
<b>CHAPTER V</b>	
<b>V. Conclusion:</b>	201

## **Chapter - I**

### ***Introduction***

# Introduction

The study of reaction rate leads to understand the steps by which a reaction takes place. The series of steps involving in reaction is called the reaction mechanism. The study off the reaction mechanism involvees a knowledge of all the details of molecular interactions in the reaction, including the change in energetics and stereochemistry with respect of internuclear distances and angles. Therefore, the chemical kinetics and its methodology are valuable means to elucidate reaction mechanism which is expected to describe the various molecular events that culminate in the formation of the final products(s).

The thermodynamics data gives the information about the feasibility or extent of the reaction while kinetic data provide the path or mechanism of reaction. Thus the kinetic data in collaboration with thermodynamic data provide the complete information of chemical reaction. The various thermodynamic parameters for activation process viz. energy of activation ( $\Delta E^\#$ ), entropy change ( $\Delta S^\#$ ), heat enthalpy change ( $\Delta H^\#$ ), free energy change ( $\Delta G^\#$ ) etc. are helpful in understanding the mechanism of a reaction. The sign and magnitude of activation parameters are also important from the mechanism view point.

There is a wide variety of reactions, which do not occur in gas phase but proceed rapidly in various solvents. The reaction in liquid phase differ markedly from reactions in the gaseous phase because

of the presence of solvent molecules, which are always in intimate contact with the reactant molecules and in fact, may often interact strongly with them. The effect of the medium on the kinetic characteristics is one of the principal means for studying liquid- phase reactions. With the variation in the solvent properties together with variation in the reagent concentration, temperature, action of light etc. one can obtain the required informations, which may be helpful in predicting the mechanism of the reaction in solution phase.

The most thoroughly investigated type of reaction in solutions are electron- transfer reactions between an oxidant and reducant and known as redox reactions. The study of the kinetics of redox reactions always remain a matter of importance and interest. The redox potential of the redox system is the main guiding factor for any redox reaction. Several oxidising and reducing agents have been used in past for the overall as well as step by step oxidation and reduction processes.

The kinetics of several redox- reactions involving a large numbers of organic and inorganic substrates by various oxidant such as, potassium- permanganate, peroxydisulphate, hydrogenperoxide, hexacyanoferrate (III), cerium (IV), Chloramine-T, Chloramine- B, bromamine- B, bromamine- T, Chromium (VI), N-bromoacetamide, N-bromosuccinimide, sodium metaperiodate etc. have been studied from mechanistic view point. The role of several transition metal-ions including platinum group metal ions viz. osmium (VIII), ruthenium (III), ruthenium (VIII), palladium (II),

platinum (IV)m irridium (III) etc. have been investigated extensively in most of the above redox reactions.

In the catalysed reactions several shortlived intermediates have been observed depending upon the various active species of the catalyst and pH of the medium and therefore , the mechanism of the catalysed reaction mostly have been found of the different from that of the uncatalysed reaction. However in most of the cases the end products were the same. The identification of the intermediate species during these investigations always remained an important factor which lead to elucidation of mechanism of catalysed reactions.

## **Platinum group metal - ions Catalysis:**

Thre is a gread blossoming of research into the chemistry of the transition metals especially in the ara of the platinum metal complexes and their use in homogenous catalysis. Despite increased financial stringency, it is still flourishing today as testified by the recently established series of international conferences and number of research papers devoted entirely to platinum metal chemistry.

Platinum group metals viz, Ru, OS, Rh, Ir, Pd and Pt are the six heaviest members of group VIII of the periodic table and are rare elements. The chemistry of these elements have some common features but there are, nevertheless, wide variation depending on different stabilities of the oxidation states, stereo - chemistry and their ability to form co-ordination and chelate complexes.

The platinum group metals have been used as catalysts for a

variety of homogenous reactions viz. hydrogenation, hydration, polymerization, isomerization, decarboxylation etc. It has been observed that a very small amount of these metal-ions (10<sup>-4</sup> to 10<sup>-7</sup> M) is sufficient to catalyse many redox reactions. Various reviews on the platinum metals catalysis and platinum metals complexes have appeared in the recent years.

Platinum group metal-ions specially palladium (II)<sup>1-8</sup>, platinum (IV)<sup>9-11</sup>, rhodium (III)<sup>14-20</sup>, have widely been used as catalysts in several redox reactions. The kinetic investigations in presence of ruthenium (III) and osmium (VIII) as catalysts have been discussed in brief in following proceedings.

## **Ruthenium (III) as Catalyst:**

Ruthenium (electronic structure = [Kr]4d<sup>7</sup> 5s<sup>1</sup>) has maximum number of ten oxidation states viz. (I) to (VIII), (-11) and (Zero). The most unstable states are (-II) whereas (III) state is more stable. The Ru (III) catalysed oxidations are most remarkable in many respects. Although the Ru (VI)<sup>21-24</sup> and Ru (VIII)<sup>25-26</sup> have also been used as a catalyst in redox reactions.

Mostly ruthenium trichloride has been taken as the source material in Ru (III) catalysed redox reactions. Ruthenium trichloride is hygroscopic in nature, readily soluble in water as well as in alcohol. The substance is sensitive to temperature and hydrolysed at 50°C to form black hydrated oxide and therefore oxide and therefore, should be stored in a refrigerator at 0°C. Ruthenium (III)

has been used as a homogenous catalyst in various redox reactions<sup>27-49</sup>. The inhibitory effect of Ru (III) on the rate of oxidation of dimethylsulfoxide (DMSO) by N-bromosuccinimide and N-bromophthalimide has also been observed<sup>50</sup>.

Depending upon medium, reactive species of the catalyst and the oxidant, a wide variety of kinetic results have been observed in ruthenium (III) catalysed reaction. Generally it has been observed that the oxidation proceeds via formation of an intermediate complex ruthenium (III)<sup>22,24,27,29-31,51-54</sup>.

However, the formation of an intermediate complex between the ruthenium (III) and the active species of the oxidant is also reported in some cases<sup>55</sup>.

## **Osmium (VIII) as Catalyst:**

The bluish-grey osmium (mp=3700°C, bp=5100°C) is the heaviest element among the platinum group metals. It is non malleable, brittle, hard and is able to scratch glass. Osmium, which was discovered by Tennat in 1803, (electronin configrutaion= ([Xe])4f<sup>14</sup>5d<sup>6</sup>s<sup>2</sup>) has various oxidation states viz. 0, +2, +3, +4, +6, +7,+8.

Osmium readily unites with oxygen. Osmium is known to forms two oxides, OsO<sub>2</sub> and OsO<sub>4</sub>, although OsO<sub>3</sub> also exists at 800-1500°C. Osmium-tetraoxide (OsO<sub>2</sub>) is thermally more stable than the dioxide osO<sub>2</sub>. Osmium-tertaoxide can be prepared by burning osmium or by oxidation of osmium solutions with nitric acid. Osmium

tetraoxide is soluble in carbon tetrachloride and alkali. Osmium tetraoxide has tetrahedral structure and is powerful oxidising agent in alkaline medium. The kinetics of various redox have been studied using osmium tetraoxide as an oxidising agent.

Osmium tetraoxide i.e. Osmium (VIII) has widely been used as a catalyst in homogenous reactions. The catalytic effect of the osmium (VIII) in various redox reactions along with the mechanism of the reactions has been described by Agarwal and Upadhyay<sup>56</sup> in form of a review. It has been observed that in some cases especially in chloramine-T oxidation the osmium (VIII) serves as the effective oxidant and itself converted to osmium (VI). The oxidant used in the reaction is utilized to regenerate osmium (VIII) from osmium (VI). After appearance of the above review further, a large number of reports<sup>57-87</sup> involving osmium (VIII) as catalyst have been appeared in the literature.

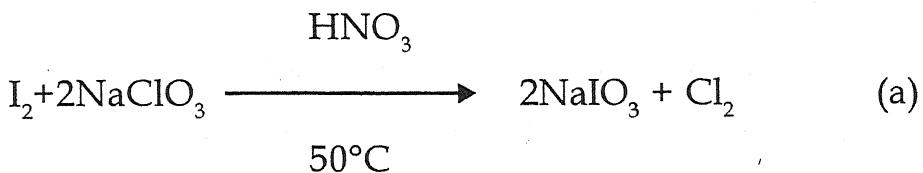
The formation of {Osmium (VIII)-Substrate} complex as an intermediate has generally been observed during the osmium (VIII) catalysed redox-reactions. However, in some cases the formation of Osmium (VIII)-Oxidant} complex as an intermediate has also been reported<sup>72,80-81</sup>.

## **Metaperiodate as Oxidant:**

In 1926 Louis Malaprade<sup>88</sup> first time used periodate as a titrimetric reagent for the indirect determination of organic and inorganic substances. Periodic acid its salts, Known as strong

oxidants, are often used in preparative organic chemistry.

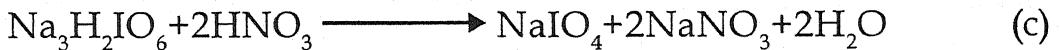
The preparation of periodate involves a suitable iodate as the starting material, which itself can be prepared by oxidation of I<sub>2</sub> with sodium chlorate as follows<sup>89</sup>,



The oxidation of iodate with chlorine gas in alkaline solution, gives sodium paraperiodate [Na<sub>3</sub>H<sub>2</sub>IO<sub>6</sub>]

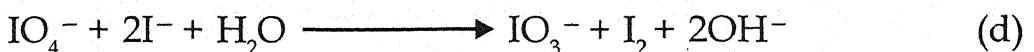


Sodium paraperiodate when treated with nitric acid, gives sodium metaperiodate (NaIO<sub>4</sub>),



Aqueous solutions of the potassium or sodium salt of metaperiodic acid is generally used in analytical or synthetic applications. The iodometric method with several modifications<sup>90-98</sup> is reported for the standardization of metaperiodate.

In buffered alkaline solutions periodate is reduced with iodide to iodate:



The iodine so formed in the reactions may be estimated with arsenite<sup>90,96</sup>.

Because periodate as well as iodate ions are colourless, redox

indicators can be used for the visual detection of the end point in direct titrations in which periodate is reduced to iodate<sup>99</sup>. When periodate is reduced to the  $I^+$  ion, the change of a chloroform or carbon tetrachloride layer may help in detection of the end point<sup>100-101</sup>. The colour, owing to the intermediately formed iodine disappears at the equivalence point, because the iodine is quantitatively oxidised to the  $I^+$  ion. The decolorisation of the blue iodine-starch solution can also periodate is reduced to iodine, the appearance of blue colour of the starch solution with iodine, serves to detect the equivalence point<sup>103</sup>. Some of the specific properties of metaperiodate have been described in brief as follows;

## **Solubility:**

Sodium metaperiodate is the most soluble among the periodate salts in water (9.3 g per 100 g water at 20°C and 12.62 g per 100 g water at 25°C)<sup>104</sup>. The solubility is greatly reduced in alkaline solution because of the formation of disodiumparaperiodate ( $Na_2H_3IO_6$ ) which is slightly soluble (0.23 gm per 100 gm water)<sup>105</sup>.

## **Stability of Aqueous solution:**

The aqueous solution of metaperiodate is stable for indefinite periods of time at room temperature and in the dark. However the solution slowly evolve ozone in the presence of light<sup>106</sup>.

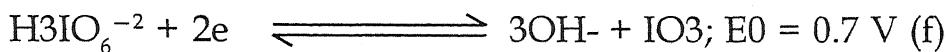
## **Standard Potentials:**

Abel and Semtana<sup>107</sup> studies the potential of the iodateperiodate

couple and observed standard reduction potential ( $E^\circ_{\text{Red}}$ ) as 1.51 V in acidic medium. On the basis of quantitatively oxidation of maganous ion ( $Mn^{+2}$ ) of periodate of permanganate, Latimer<sup>107</sup> estimated  $E^\circ$  value for the periodate-iodate couple as 1.6 V in scid solution.

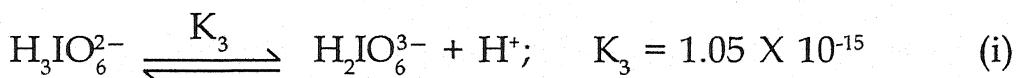
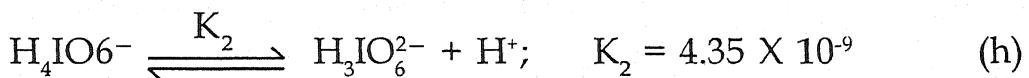
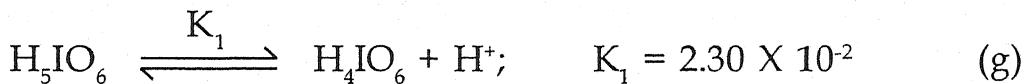


However, in alkaline solution the lower value of  $E_0$  ( $=0.7$  V) has been observed.

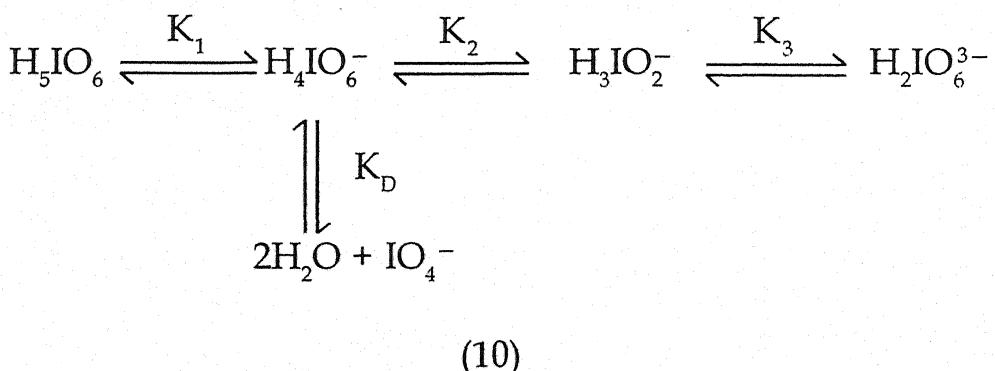


## **Ionization:**

The apparent ionization constants for periodic acid<sup>108</sup> are shown as below;



The overall hydration equilibria relating  $\text{H}_4\text{IO}_6^-$  to  $\text{IO}_4^-$  may be represented by the following scheme,



On the basis of above equilibria, Crouthmel et al<sup>109</sup> determined the true ionisation constants and the dissociation constants relating to the  $\text{H}_4\text{IO}_6^-$  and  $\text{IO}_4^-$  species as follows,

$$\frac{a_{\text{H}^+} a_{\text{H}_4\text{IO}_6^-}}{a_{\text{H}_5\text{IO}_6}} K_1 = 5.1 \times 10^{-4} \quad (\text{j})$$

$$\frac{a_{\text{H}^+} a_{\text{H}_3\text{IO}_6^{2-}}}{a_{\text{H}_4\text{IO}_6^-}} K_2 = 2.0 \times 10^{-7} \quad (\text{k})$$

$$\frac{a_{\text{IO}_4^-}}{a_{\text{H}_4\text{IO}_6^-} a_{\text{H}_2\text{O}}} K_D = 40 \quad (\text{l})$$

Ivanova and Neumann<sup>110</sup> observed a negligible effect of temperature on the ionization constants.

## Structure of periodates:

Hazelwood<sup>111</sup> has shown by X-ray diffraction that the periodate monoanion  $\text{IO}_4^-$  is tetrahedral. The dianion ( $\text{H}_3\text{IO}_6^{2-}$ ) is octahedral<sup>112-113</sup>. The tetrahedral structure of univalent periodate ion has also been confirmed by the infrared-spectra of periodates in  $\text{D}_2\text{O}$  and the infrared spectra<sup>114</sup> of silver periodate.

## Effect of pH:

The active species of periodate is sensitive to pH. At  $\text{pH} = 1.2$ , periodate exists 80% in unionised form and 20% in monoionised

form. At pH = 2.3 the unionised and ionised form have been found to be 35% and 65%, respectively<sup>115</sup>. The predominant species in the aqueous medium is the mono-anionic species ( $\text{IO}_4^-$ ) which has also been confirmed from Raman spectroscopy by Seibert<sup>116</sup>. However, Symons<sup>117</sup> prefer  $\text{H}_4\text{OI}_6^-$  to  $\text{IO}_4^-$  on the basis of spectral evidence. Buist and Lewis<sup>118</sup> reported a dimeric species  $(\text{O}_4\text{I}-\text{O}-\text{IO}_4)^4$  in the aqueous solution of increasing concentration of periodate from  $10^{-5}$  to  $10^{-2}\text{M}$  at pH = 11.4.

## **Metaperiodate Oxidation:**

Metaperiodate is well known oxidising agent. The oxidation of various organic and inorganic substances by  $\text{IO}_4^-$  have extensively been investigated in acidic, alkaline, and neutral aqueous media. However, periodic acid and periodates oxidise many substances at high temperatures, hence these oxidations lose their analytical significance at the high temperatures. The velocity of the oxidation of organic substances by periodate also depends on the pH of the medium, for example-oxidations of polyhydroxy compounds proceed best at pH 4 while that of  $\alpha$ -amino acids proceed at pH range 7-9. The oxidation can also be influenced by the action of light<sup>119</sup>. Oxidations with periodic acid or periodate are usually carried out in aqueous solution, however, organic viz. methanol, ethano, tert-butanol, dioxan, acetic acid etc. have also been used.

Periodate oxidation is undoubtedly one of the most widely used reactions in synthetic organic chemistry. The reaction has found its

greatest application in the field of carbohydrate chemistry, both for the purpose of investigating molecular structure of carbohydrates and for analytical purpose. Hughes and Nevell<sup>120</sup> found that in the oxidation of glucose the rate of periodate consumptions was faster than the rate of product formation; this was interpreted as being due to a build-up of intermediate species. In periodate oxidation of carbohydrates the intermediate products are oftenly malonic acid or malondialdehyde.

The kinetics of uncatalysed sodium metaperioate oxidation of various substrates such as p-chloraniline<sup>121</sup>, 2-hydroxynaphthaldehyde<sup>122</sup>, p-bromoaniline<sup>123\*</sup>, o-chloroaniline<sup>124</sup>, p-phenetidine<sup>125</sup>, glycerin<sup>126</sup>, 2-amino-5aryl-1,3,4-oxadiazale<sup>127</sup>, N-N-dimethyl-p-toluidine<sup>132</sup>, m-toludine<sup>133</sup> and isocarvacrol<sup>134</sup> have been studied and mechanism of the reactions have been proposed.

Although  $\text{IO}_4^-$  is a powerful oxidising agent both in acidic and basic media, it is not potent enough to oxidise various substrates. However in the presence of catalytic amount of transition metal ions, viz. palladium (II)<sup>135</sup>, ruthenium (VIII)<sup>136</sup>, Mn(II)<sup>137</sup>, chromium (VI)<sup>138</sup>, ruthenium(III)<sup>139-155</sup> and osmium (VIII)<sup>83-87</sup> etc. these oxidations are facile and these redox processes have considerable interest.

Sodium metaperiodate oxidation of various organic and inorganic compounds has shown a wide variation of kinetic results due to different reactive species of metaperiodate. Ruthenium(III) and osmium (VIII) also exist in different reactive species depending upon the pH of the medium. The oxidation of reducing sugars by

metaperiodate does not proceed of platinum group metal ions viz. ruthenium(III) or osmium (VIII) the reactions proceed with a measurable speed at low temperatures. The kinetic investigations on oxidation of reducing sugars viz. maltose and sorbose by metaperiodate in presence of ruthenium (VIII) have shown a complicated and interesting results. The reactions were zero order in substrate. However, in presence of ruthenium(III) preliminary studies on the same reactions made by us, showed a first dependence of rate with respect to substrate and variation in order with respect to oxidant. Therefore, it is proposed to study the detail kinetics of oxidation of some reducing sugars by sodium metaperiodate in presence of catalysts viz. ruthenium(III) and osmium(VIII) in order to compare the catalytic activity of the both the catalysts in the same reaction.

The kinetic results for the oxidation of reducing sugars viz. glucose, fructose and galactose (monosaccharides), maltose and lactose (disaccharides) by sodium metaperiodate in the presence of ruthenium(III) and osmium(VIII) as catalysts are reported in chapter, III and IV, respectively.

The mechanism for the oxidation reaction has been proposed in each case and corresponding rate laws have been derived and discussed at the end of respective chapter. Chapter V consists a comparative study of the kinetic results obtained in presence of the two catalysts viz. ruthenium (III) and osmium(VIII).

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## **Chapter - II**

### ***Materials and Techniques Used***

# Experimental

## Preparation of solutions:

1. An Aqueous solution of sodium metaperiodata ( $\text{NaIO}_4$ ) was prepared always fresh from (E. Merk) sample by direct weighing. The solution was standardised by the iodometric method<sup>1</sup> and was preserved in dark bottles to prevent photochemical deterioration.
2. Aqueous solutions of D(+) glucose (CDH), D(-) fructose, D(+) galactose and D(+) lactose (s.d. Fine), D(+) maltose (Qualikem) were direct prepared from analytical grade samples.
3. The stock solution of ruthenium trichloride ( $\text{RuCl}_3$ )  $15.2 \times 10^{-3}$  mol dm<sup>-3</sup>) was prepared<sup>2</sup> by dissolving 1.0. gm. of sample of  $\text{RuCl}_3$  (Thomas Baker) in 25 ml of HCl (0.01M) and then diluting it to 250 ml with doubly distilled water. the stock solution was stored in black coated bottles to prevent photochemical decomposition.
4. The ruthenium (III)<sup>3</sup> content in the stock solution was checked spectrophotometrically from time to time. The hundreds of more time dilute solution of the stock solution of the catalyst was used in the reaction mixtures.
5. Aqueous solution of alkali was prepared by dissolving NaOH (AR, BDH) in doubly distilled water and was standardised by titrating it against standard oxalic acid solution using

phenolphthalein as an indicator.

6. For ionic strength studies, aqueous solution of sodium perchlorate was prepared from A.R. grade sample.
7. An aqueous stock solution of sodiumthiosulphate (A.R. BDH) was used for estimation of sodium metaperiodate. A 10% wolutiion of potassium iodide (Thomas Baker) was always prepared fresh to liberate iodine.
8. Freshly prepared 1% starch solution was used for iodometric titration.

Other reagents used during the course of investigation were of AR grad. All solutions were prepared in double distilled water. Stills used, were all made of Jena ofr corning glass. REaction flasks were coated black from outside to avoid photochemical decomposition of reactants.

## **Experimental Method:**

Appropriate quantities of the solution of substrate, sodium hydroxide and catalyst ( $\text{RuCl}_3$ ) were taken in a 100 ml Jena glass vessel. Requisite amount of double distilled water was added so that the total volume of reaction mixture would become 50 ml after adding the solution of sodium metaperiodate (in separate flasks) were now placed in a thermostatic water bath maintained at the disired temperature within the range  $\pm 0.1^\circ\text{C}$ . The reaction mixture and oxidant solution solution were allowed to attain the temperature

of the water bath. The reaction was started by adding the requisite amount of sodium metaperiodate solution to the reaction vessel.

The kinetics were followed by determining the unreacted amount of sodium metaperiodate. An aliquot of 5 ml of reaction mixture was withdrawn from reaction vessel at a definite time interval and was transferred to titrating flask containing 5 ml of 3N. $\text{H}_2\text{SO}_4$  and 5 ml of 10% KI solution. The solution was then titrated with sodium thiosulphate (hypo) solution using starch as indicator to determine the amount of unreacted sodium metaperiodate.

## **Determination of the Order of Reaction:**

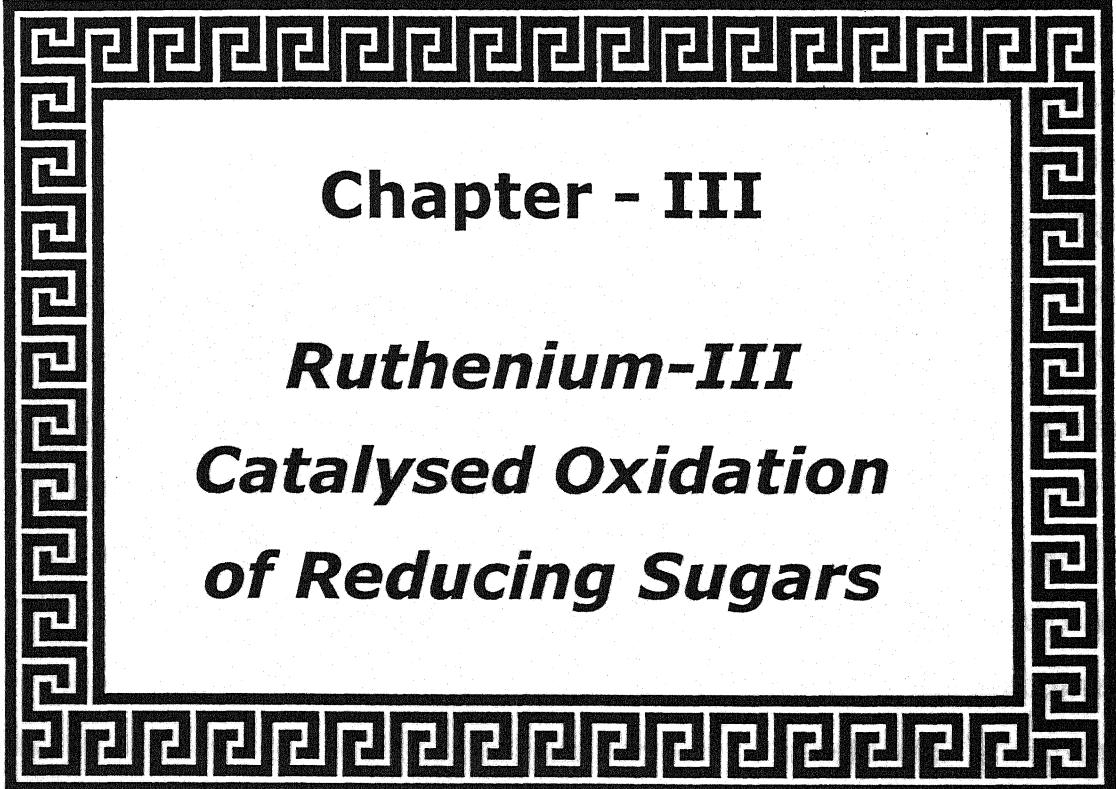
During the investigations of concentration of the solution of sodium metaperiodate was always kept at least eight times dilute than the concentration of the reducing substrate solution to maintain pseudoorder conditions.

In ruthenium (III) Catalysed reactions,  $\log$  [sodium metaperiodate] versus time plots were linear suggesting a first order dependence of rate with respect of oxidant. Therefore, the pseudo-first order rate constants in sodium metaperiodate were obtained from the slopes (slope =  $k_{\text{obs}}/2.303$ ) of these straight lines plotted between  $\log (a-x)$  versus time (where  $(a-x)$  correspond to unreacted amount of sodium metaperiodate, at any time  $t$ ). In place of  $(a - x)$  the direct titre value i.e. amount of hypo required for titration of 5 ml of reaction mixture of different time intervals has been taken in the various plots.

Effect of [reactants], [catalyst],  $[\text{OH}^+]$ , ionic strength, solvent, products and temperature on the rate has been investigated in each case. The products have been identified and the stoichiometry of the reactions has been also studied. The systematic kinetic data are tabulated in each case and mechanism has been discussed in the end of chapter. In some cases e.g. ionic strength effect and temperature effects, the value of observed rate constants have only been given for the sake of brevity.

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## **Chapter - III**

### ***Ruthenium-III***

### ***Catalysed Oxidation***

### ***of Reducing Sugars***

# **Oxidation of Reducing Sugars by $\text{IO}_4^-$ in Presence of Ruthenium**

## **(III) A. Introduction :**

The carbohydrates (sugars) are important biochemical compounds as they play both a structural role and a mean of energy storage. The interesting as they are, some times, slow to equilibrate and also oxidise in presence of metal ions. The Kinetics of the oxidation of reducing sugars by various oxidants such as N-bromosuccinimide<sup>1-10</sup>, potassium bromate<sup>11-12</sup>, potassium permanganate<sup>13-14</sup>, hexachloroirridate<sup>15</sup>, cromic acid<sup>16</sup>, hexacyanoferrate (III)<sup>17-20</sup>, cerium (IV)<sup>21-27</sup>, iron (III)<sup>28</sup>, copper (II)<sup>29-30</sup>, t-butylhypochlorite<sup>31</sup>, manganese<sup>32</sup>, persulphate ion<sup>33</sup>, chloramine-B<sup>34-39</sup>, bromamine-B<sup>40</sup>, bromamine-T<sup>41-43</sup>, chloramine -T<sup>44-49</sup>, chromium (IV)<sup>50</sup>, N -bromoacetamide<sup>51-53</sup>, sodium metaperiodate<sup>54-56</sup> have been studied and mechanism of the reactions have been proposed. The effect of various catalysts viz. Thallium (III)<sup>57</sup>, iron (II)<sup>58</sup>] vanadium (V)<sup>59-63</sup>, cobalt (II)<sup>64</sup>, nickel (II)<sup>20</sup>, osmium (VIII)<sup>65</sup>, palladium (II)<sup>5-8,52</sup>, iridium (III)<sup>1,4,26,50</sup>, ruthenium (III)<sup>2,53,55-56</sup> and ruthenium (VIII)<sup>54</sup> etc. on the rate of oxidation has also been studied. Generally, the reaction proceed via formation of an intermediate complex between the substrate and the catalyst. It has been observed that among the platinum group metal-ions, ruthenium (III) wavers as a remarkable effective catalyst. The catalytic role of ruthenium (III) in several redox reactions involving oxidants viz.

cerium (IV), hexacyanoferrate (III), thallium (III), N-bromosuccinimide, chloramine - B etc. has been reviewed by N.D. Kandpal *et al.*<sup>66</sup>.

The kinetics of ruthenium (VIII) catalysed oxidation of some reducing sugars giz. sorbose and maltose by sodium metaperiodate<sup>54</sup> have been studied in alkaline medium. The reactions followed a first order dependence of rate of oxidation with respect to each  $[\text{NaIO}_4]$ ,  $[\text{Ru(VIII)}]$  and  $[\text{OH}^-]$  at their lower concentrations of the reactants, and a zero order dependence of rate with respect to the substrate. Variation of ionic strength of the medium showed a negligible effect of the rate of oxidation.

During the preliminary experiments in the laboratory, it was observed that the kinetic results for the oxidation of reducing sugars by sodium metaperiodate in presence of ruthenium (III) ion were different from those reported by Gupta *et al.*<sup>54</sup> for the oxidation of sugars by meaperiodate in presence of ruthenium (VIII) ion. The observed first order dependence of rate with respect to substrate in our experiments clearly indicated the different behaviour of two species of the catalyst, i.e. rethenium (III) and ruthenium (VIII). Therefore, In order to throw the light on the catalytic role of ruthenium (III) during periodate oxidation of reducing sugars, the kinetics of the reactions have been investigated in details and the results are reported in this chapter. The oxidation of five reducing sugars giz. fructose, glucose, galactose, maltose and lactose have been studied. The effect of substrate, oxidant, catalyst, pH,

temperature etc. has been studied on the rate of reaction and a mechanism consistent with kinetic data has been proposed and discussed at the end of the chapter.

### **III B. Stoichiometry and Identification of Products:**

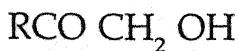
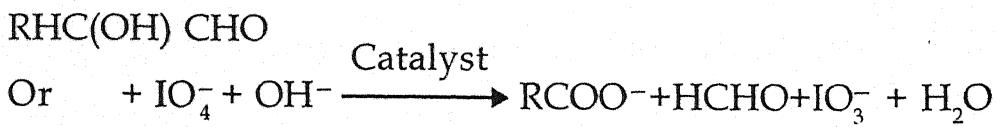
The reaction products have been identified in both the conditions i.e. under the kinetic conditions where, [substrate] > [oxidant] and under the stoichiometric conditions where, [oxidant] > [substrate].

#### ***Under kinetic Conditions:***

The reaction mixtures were analysed periodically for identification of products under the kinetic conditions. Several reaction mixtures were prepared keeping  $(\text{RuCl}_3)$  and  $[\text{NaOH}]$  at fixed concentration. After the complete reaction, the reaction mixture was taken out from the reaction vessel and product was tested.

The presence of formaldehyde and corresponding lower acid of the reducing sugar was detected by spot test<sup>67</sup>. The presence of formaldehyde was confirmed by formation of 2-4 DNP derivative and comparing its m.p. and TLC with that of the authentic sample. Thus under the kinetic conditions, the reducing sugar oxidised to formaldehyde and corresponding lower acid.

The results may be represented as,



where R represents  $\text{CHOH} (\text{CHOH})_2 \text{CH}_2\text{OH}$  in case of fructose, glucose and galactose and  $\text{CHOHC} (\text{OR}') \text{HCHOH} \text{CH}_2\text{OH}$  in case of maltose and lactose where  $\text{R}'$  is nonreducing glucose and galactose unit of maltose and lactose, respectively.

The formaldehyde as oxidation product of aldoses during periodate oxidation is also reported<sup>68</sup>.

### ***Under stoichiometric Conditions:***

The stoichiometry of the reaction was also studied in the presence of excess of oxidant i.e. sodium metaperiodate. Different sets of reaction mixtures containing a known excess of  $[\text{IO}_4^-]$  over [Reducing sugar] and at a fixed concentrations of catalyst and  $\text{OH}^-$  were kept at  $40^\circ\text{C}$  for 72 hours and then analysed. The unreacted oxidant was determined iodometrically. Estimation of unreacted  $\text{IO}_4^-$  showed that one mole of monosaccharide (glucose, galactose and fructose) consumes two moles of  $\text{IO}_4^-$  while one mole of disaccharide (maltose and lactose) consumes more than three moles of  $\text{IO}_4^-$ .

The qualitative analysis of the product (TLC) indicated the presence of a mixture of formic acid and corresponding lower acid of reducing sugar. These products are indicative for  $\text{C}_1-\text{C}_2$  splitting.

Thus it seems that the formaldehyde, which is one of the oxidation products under the kinetic conditions, is further oxidised in presence of excess of oxidant. This result in a more than 1:1 stoichiometry between substrate and  $\text{IO}_4^-$  in case of monosaccharides. However in case of disaccharide one of the initial

product is a monosaccharide which will be further oxidised in excess of oxidant and thus more than 1:2 stoichiometry between substrate and  $\text{IO}_4^-$  is expected which has also been observed experimentally.

### **III C. Effect of $\text{IO}_4^-$ on the Rate of Oxidation:**

In order to determine the dependence of reaction rate of  $[\text{IO}_4^-]$ , the kinetic runs were made for oxidation of various reducing sugars at several initial concentrations of  $[\text{IO}_4^-]$ . The concentrations of reducing sugar, catalyst and NaOH were kept constant. The amount of hypo required for titration of 5 ml of reaction mixture at different time intervals for various kinetic runs are presented in Tables III-1 to III-5.

It was observed that  $\log (a-x)$  versus time plots were linear upto 80% of the reactions, suggesting a first order dependence of rate with respect to sodium metaperiodate.

The results are represented graphically in Figures III C-1 to III C-5.

The pseudo-first order rate constants in sodium metaperiodate ( $k_{\text{obs}}$ ) evaluated from slopes of the straight lines plotted between  $\log (a-x)$  versus time (Figures III C-1 to III C-5) are summarised in Table III C-1.

It is observed from Figures (III C - 1 to III C-5) that during a particular kinetic run, the plot of  $\log (a-x)$  versus time remains linear suggesting first order dependence of the rate with respect of  $[\text{IO}_4^-]$ . However an increases in initial  $[\text{IO}_4^-]$  (Table III C-1), resulted in a decrease in the observed pseudo-first order rate constant.

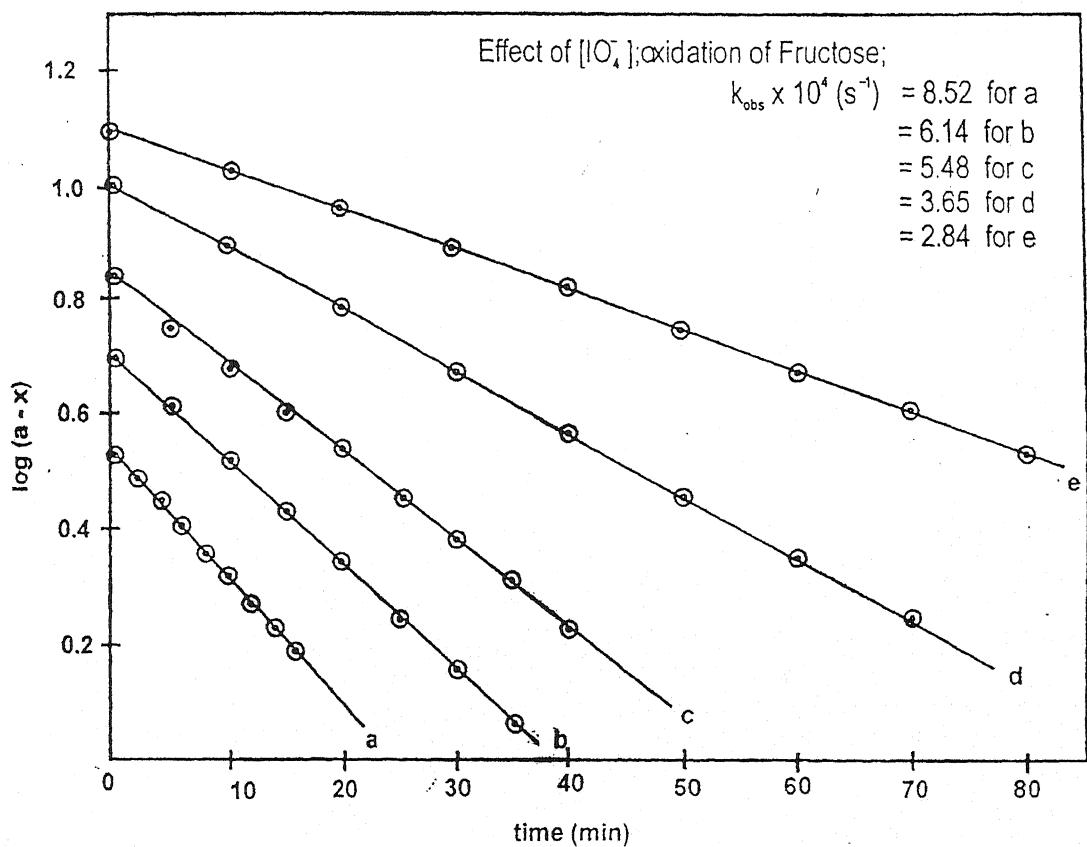


Fig. III C - 1 : Pseudo- first order plots at  $40^\circ\text{C}$

$[S] = 2.0 \times 10^{-2}$ ,  $[\text{OH}^-] = 0.1$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ , and  
 $[\text{IO}_4^-] = 1.0, 1.5, 2.0, 3.0$  and  $4.0 \times 10^{-3}$ ,  
 in a, b, c, d, and e, respectively  
 Concentrations are in  $\text{mol dm}^{-3}$ .

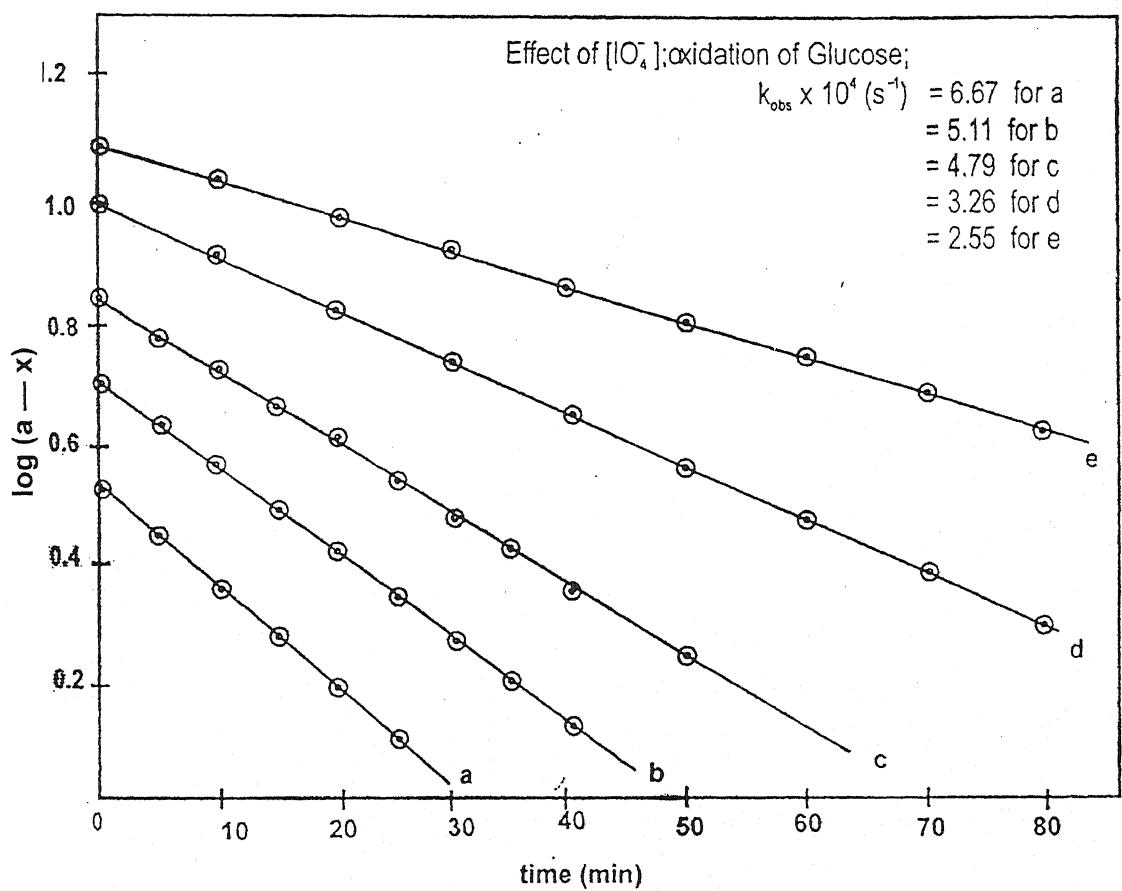


Fig. III C - 2 : Pseudo- first order plots at 40°C

$[S] = 2.0 \times 10^{-2}$ ,  $[OH^-] = 0.1$ ,  $[RuCl_3] = 3.0 \times 10^{-4}$ , and  
 $[IO_4^-] = 1.0, 1.5, 2.0, 3.0$  and  $4.0 \times 10^{-3}$ ,  
 in a, b, c, d, and e, respectively  
 Concentrations are in  $mol\ dm^{-3}$ .

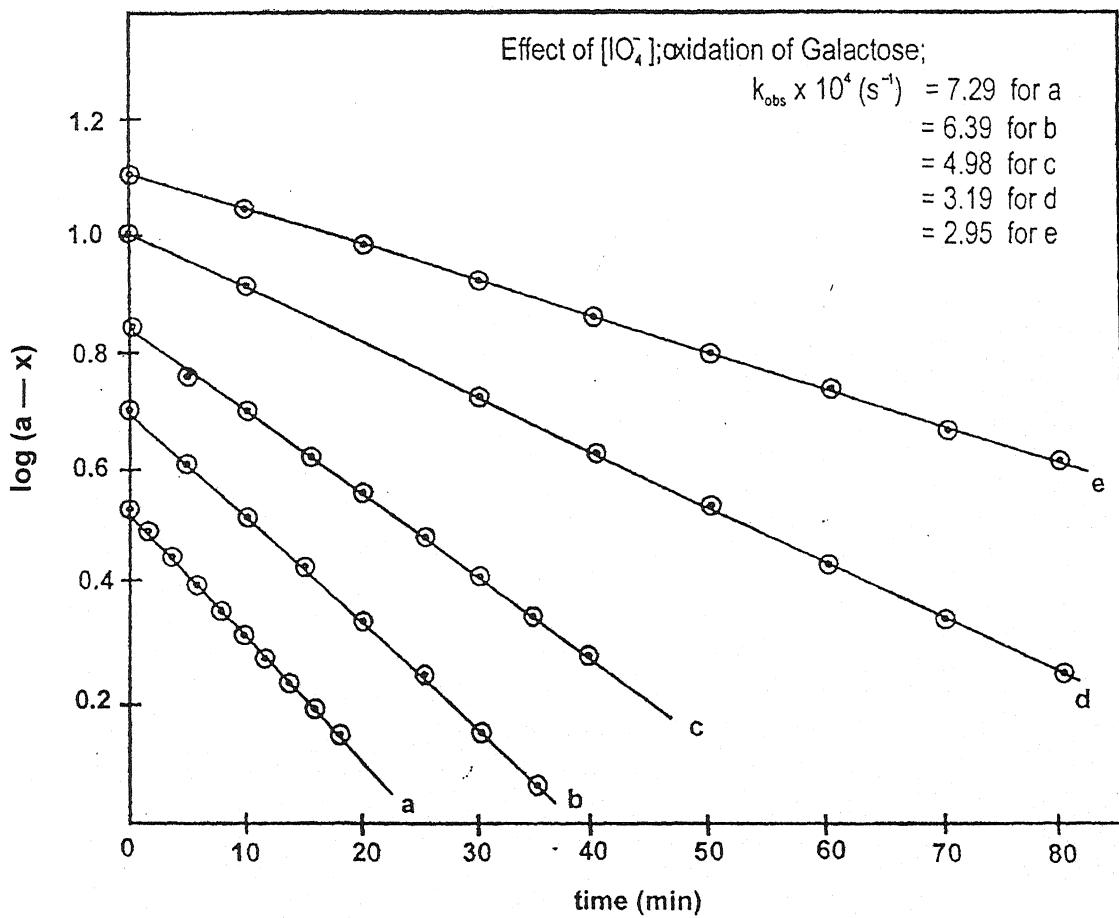


Fig. III C - 3 : Pseudo- first order plots at  $40^\circ\text{C}$

$[\text{S}] = 2.0 \times 10^{-2}$ ,  $[\text{OH}^-] = 0.1$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ , and  
 $[\text{IO}_4^-] = 1.0, 1.5, 2.0, 3.0$  and  $4.0 \times 10^{-3}$ ,  
 in a, b, c, d, and e, respectively  
 Concentrations are in  $\text{mol dm}^{-3}$ .

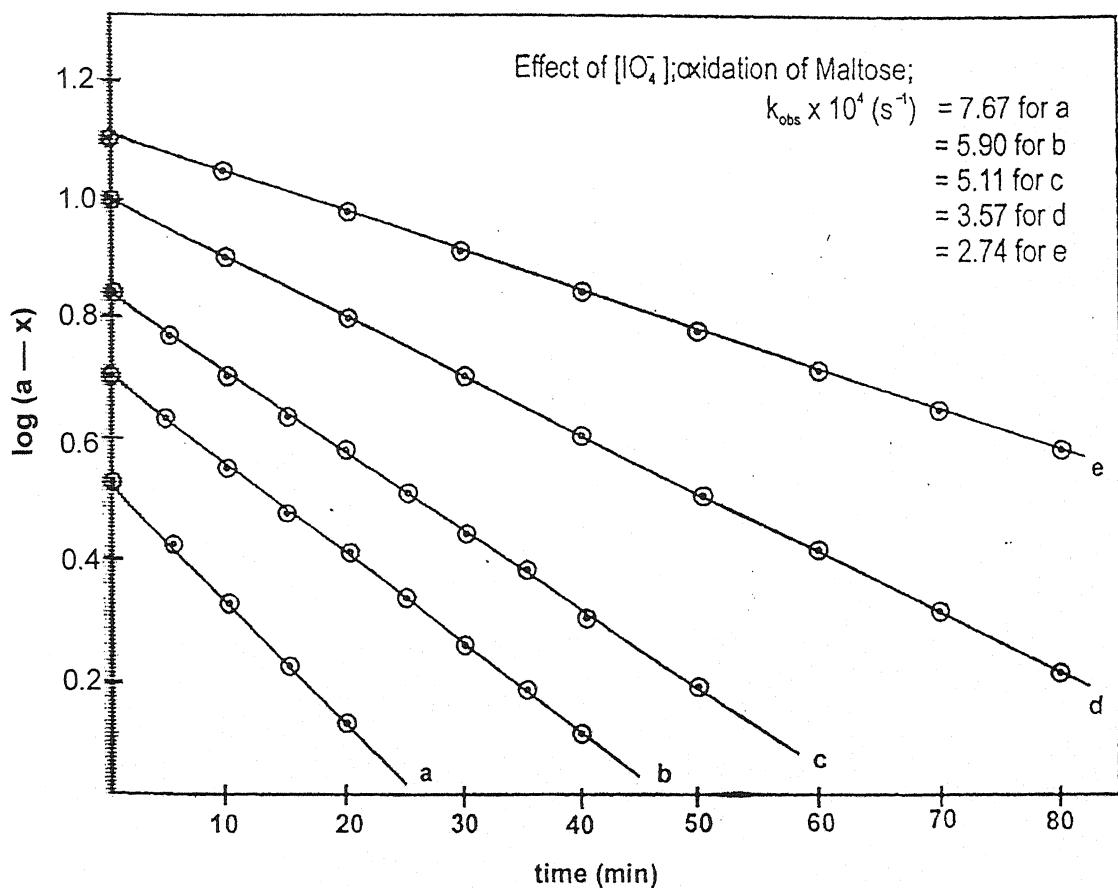


Fig. III C - 4 : Pseudo- first order plots at 40°C

$[\text{S}] = 2.0 \times 10^{-2}$ ,  $[\text{OH}^-] = 0.1$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ , and  
 $[\text{IO}_4^-] = 1.0, 1.5, 2.0, 3.0$  and  $4.0 \times 10^{-3}$ ,  
 in a, b, c, d, and e, respectively  
 Concentrations are in  $\text{mol dm}^{-3}$ .

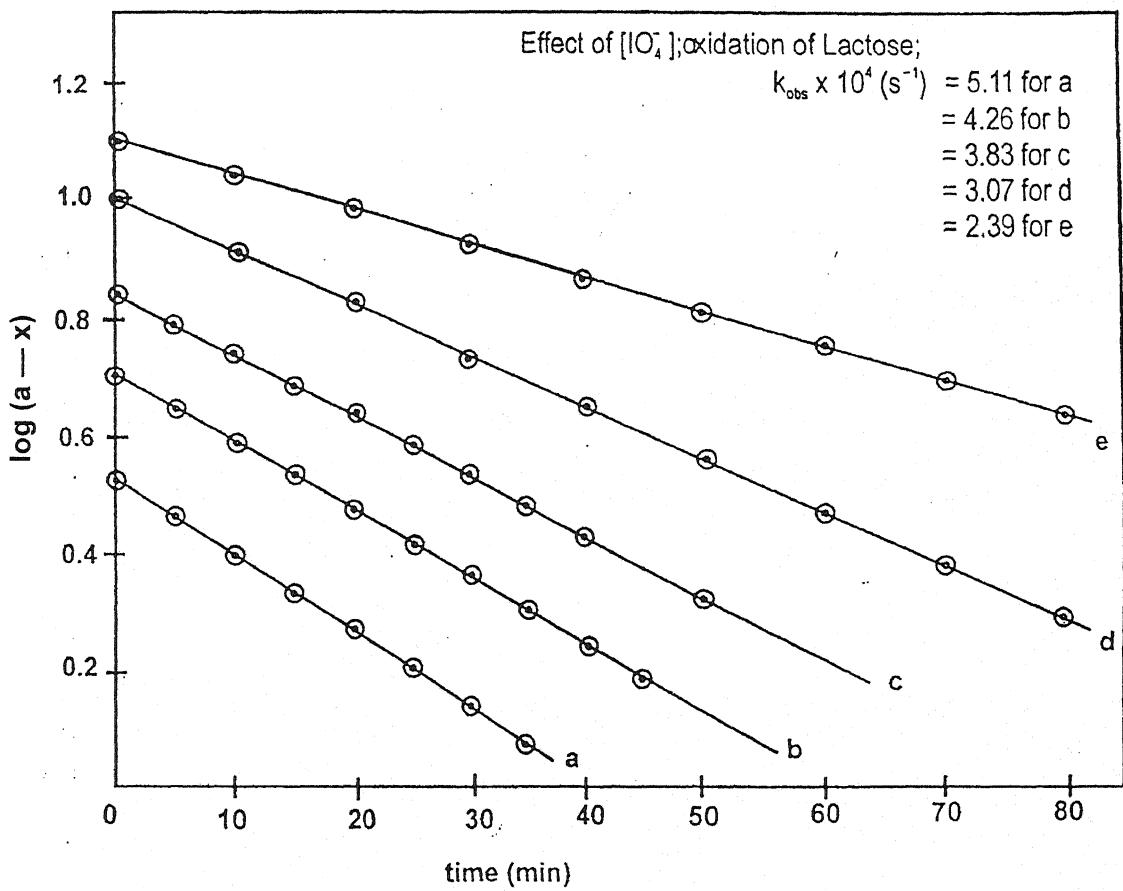


Fig. III C - 5 : Pseudo- first order plots at 40°C

$[S] = 2.0 \times 10^{-2}$ ,  $[OH^-] = 0.1$ ,  $[RuCl_3] = 3.0 \times 10^{-4}$ , and  
 $[IO_4^-] = 1.0, 1.5, 2.0, 3.0$  and  $4.0 \times 10^{-3}$ ,  
 in a, b, c, d, and e, respectively  
 Concentrations are in mol dm<sup>-3</sup>.

### **III.D. Effect of [Substrate] on the rate of Oxidation:**

To observe the effect of substrate on the rate of oxidation, the reactions were investigated at several initial concentrations of each reducing substrate. The concentrations of other reactants viz. sodium metaperiodate, ruthenium trichloride ( $\text{RuCl}_3$ ) and sodium hydroxide were kept constant as reported in tables. The amount of hypo (V, in ml) required for titration of 5 ml of reaction mixture at different time intervals for various kinetic runs are presented in Tables - III-6 to III-10. The pseudo-first order plots i.e. plots of  $\log (a-x)$  versus time at various initial concentrations of reducing sugars are represented graphically in Figures III D-1 to III D-5.

**Table - III C - 1 : Effect of [Sodium metaperiodate] on the rate constants at 40°C**

$[\text{IO}_4^-] \times 10^3 \downarrow$	$\text{FR} (\text{A}) \downarrow$	$\text{GL} (\text{B}) \downarrow$	$\text{GA} (\text{C}) \downarrow$	$\text{MA} (\text{D}) \downarrow$	$\text{LA} (\text{E}) \downarrow$	$(k_{\text{obs}}) \times 10^4 \text{ (s}^{-1}\text{)}$
1.0	8.52	6.67	7.29	7.67	5.11	
1.5	6.14	5.11	6.39	5.90	4.26	
2.0	5.48	4.79	4.98	5.11	3.83	
3.0	3.65	3.26	3.19	3.52	3.07	
4.0	2.84	2.55	2.95	2.74	2.39	

(48)

$[\text{Substrate}] = 2.0 \times 10^{-2}$ ;  $[\text{OH}^-] = 0.10$  for A, B and C; 0.20 for D and E;  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ .

The concentration of reactants are in mol  $\text{Dm}^{-3}$ .

The values of ( $k_{obs}$ ) evaluated from the slopes of linear plots between  $\log (a - x)$  versus time (Figures - IIID - 1 to III D-5) at various initial concentrations of the substrate are summarized in Table - III D-1.

It is observed from Table - III D-1 – that the  $k_{obs}$  increases with an increase in [Reducing sugar]. A plot of ( $k_{obs}$ ) versus [Reducing sugar] (Figure – III D-6) showed a deviation from linearity at higher [Reducing sugar] suggesting that order of reaction in reducing substrate decreases from unity. Further, a plot of ( $1/k_{obs}$ ) versus  $1/[Reducing sugar]$  (Figure – III D-7) was linear with a positive intercept suggesting a Michaelis - Menten type kinetics and confirming that order of reaction in substrate decreases from unity to zero at higher substrate concentration.

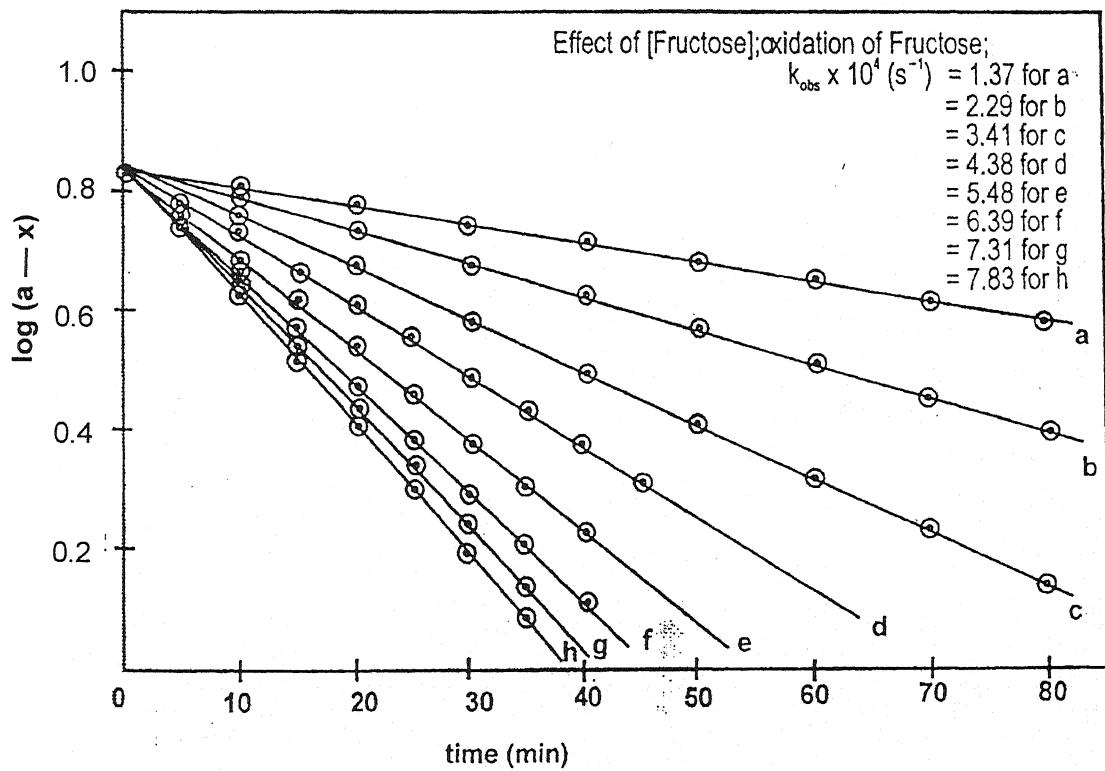


Fig. III D - 1 :Pseudo- first order plots at 40°C

$[\text{IO}_4^-] = 2.0 \times 10^{-2}$ ,  $[\text{OH}^-] = 0.1$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ ,  
 $[\text{S}] = 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0$  and  $5.0 \times 10^{-2}$ ,  
 in a, b, c, d, e and f respectively  
 Concentrations are in  $\text{mol dm}^{-3}$ .

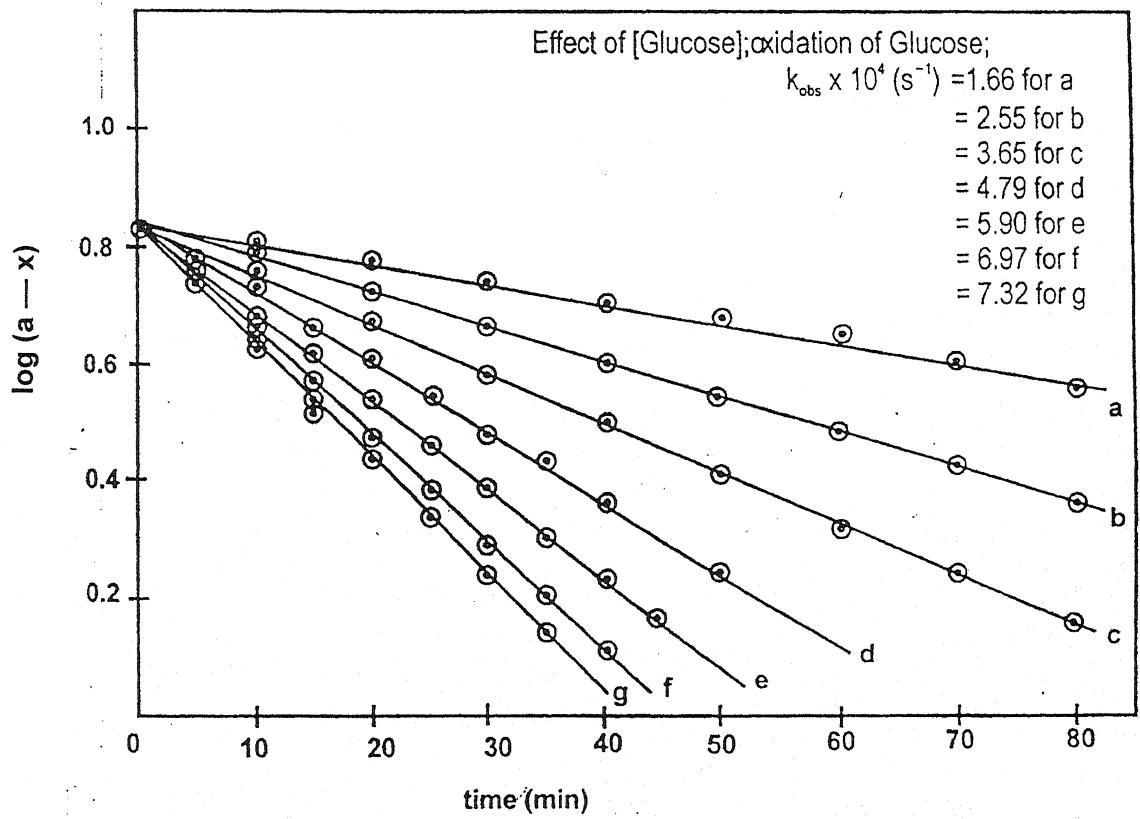


Fig. III D - 2 :Pseudo- first order plots at 40°C

$[\text{IO}_4^-] = 2.0 \times 10^{-2}$ ,  $[\text{OH}^-] = 0.1$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ ,  
 $[\text{S}] = 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0$  and  $5.0 \times 10^{-2}$ ,  
in a, b, c, d, e and f respectively  
Concentrations are in  $\text{mol dm}^{-3}$ .

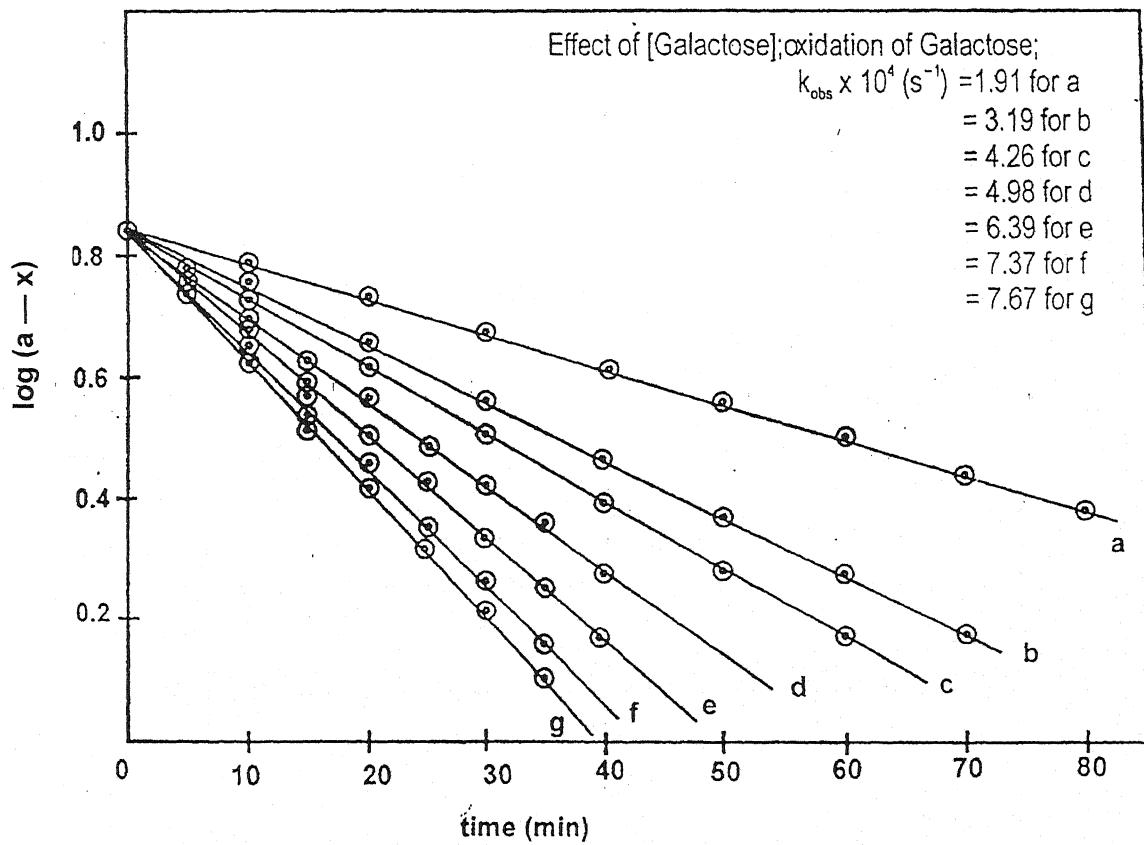


Fig. III D - 3 :Pseudo- first order plots at 40°C

$[\text{IO}_4^-] = 2.0 \times 10^{-2}$ ,  $[\text{OH}^-] = 0.1$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ ,  
 $[\text{S}] = 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0$  and  $5.0 \times 10^{-2}$ ,  
 in a, b, c, d, e and f respectively  
 Concentrations are in  $\text{mol dm}^{-3}$ .

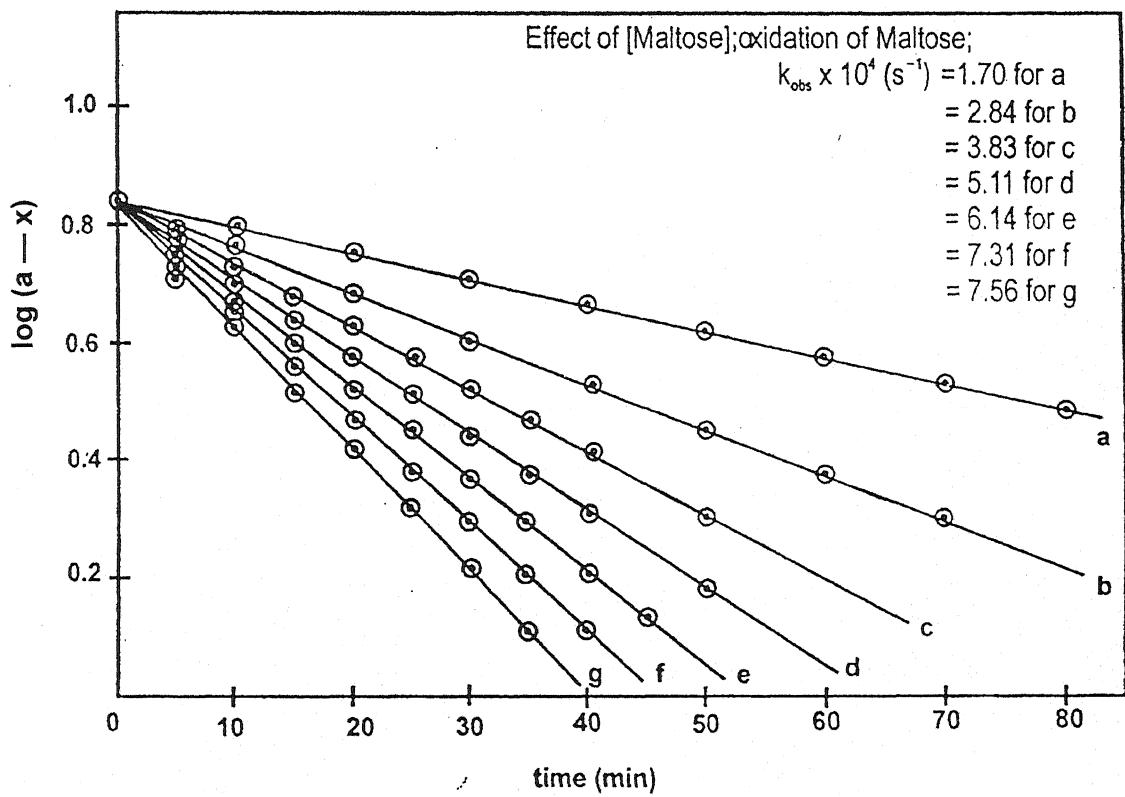


Fig. III D - 4 :Pseudo- first order plots at 40°C

$[\text{IO}_4^-] = 2.0 \times 10^{-2}$ ,  $[\text{OH}^-] = 0.1$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ ,  
 $[\text{S}] = 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 \text{ and } 5.0 \times 10^{-2}$ ,  
in a, b, c, d, e and f respectively  
Concentrations are in  $\text{mol dm}^{-3}$ .

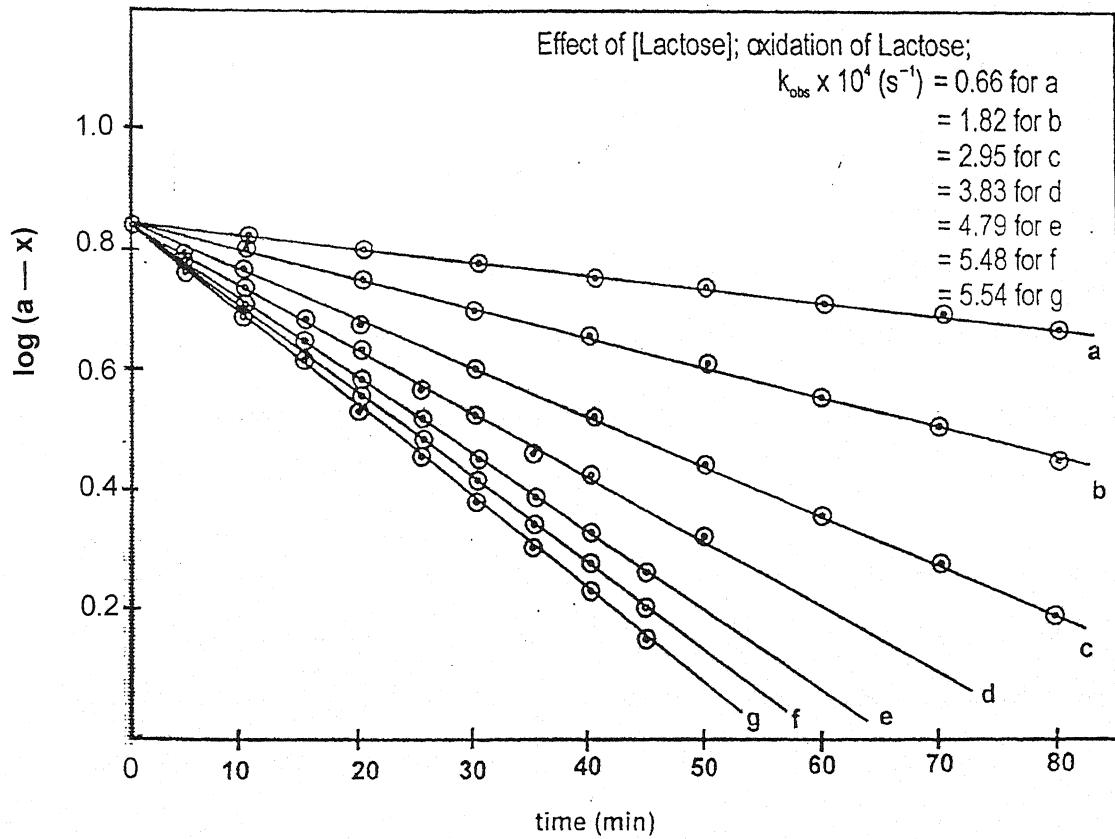


Fig. III D - 5 :Pseudo- first order plots at 40°C

$[\text{IO}_4^-] = 2.0 \times 10^{-2}$ ,  $[\text{OH}^-] = 0.1$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ ,

$[\text{S}] = 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0$  and  $5.0 \times 10^{-2}$ ,

in a, b, c, d, e and f respectively

Concentrations are in mol dm<sup>-3</sup>.

### **III. E. Effect of [Alkali] on the Rate of Oxidation:**

In order to determine the dependence of the rate of oxidation on the alkali concentration, the reactions were studied at different initial concentrations of the sodium hydroxide keeping at fixed ionic strength (as mentioned in teh Tables III-11 to III-15) maintained by the addition of sodium perchlorate ( $\text{NaClO}_4$ ). The amount of  $\text{NaOH}$  required to neutralise  $\text{HCl}$  already present in the catalyst was taken into account. The concentrations of other reactants viz. sodium metaperiodate, reducing sugars and catalyst were kept constant.

The amount of hypo required for titration of 5 ml of reaction mixtures at different time intervals for various kinetic runs are reported in Tables III- 11 to III-15.

The plots of  $\log (a-x)$  versus time i.e. pseudo first order plots for various kinetic runs in case of each reducing sugar are represented graphically in Figures – III E-1 to III E-5.

**Table - III D - 1 : Effect of [Substrate] on the rate constants at 40°C**

$[IO_4^-] \times 10^2 \downarrow$	$FR(A) \downarrow$	$GL(B) \downarrow$	$(k_{obs}) \times 10^4 (s^{-1})$	$GA(C) \downarrow$	$MA(D) \downarrow$	$LA(E) \downarrow$
0.5	2.29	1.66	1.91	1.70	0.66	
1.0	3.41	2.55	3.19	2.84	1.82	
1.5	4.38	3.65	4.26	3.83	2.95	
2.0	5.48	4.79	4.98	5.11	3.73	
3.0	6.39	5.90	6.39	6.14	4.79	
4.0	7.31	6.97	7.37	7.31	5.48	
5.0	7.83	7.32	7.67	7.56	5.54	

(56)

$[IO_4^-] = 2.0 \times 10^{-3}$ ;  $[OH^-] = 0.10$  for A, B and C; 0.20 for D and E;  $[RuCl_3] = 3.0 \times 10^{-3}$ .

The concentration of reactants are in mol  $Dm^{-3}$ .

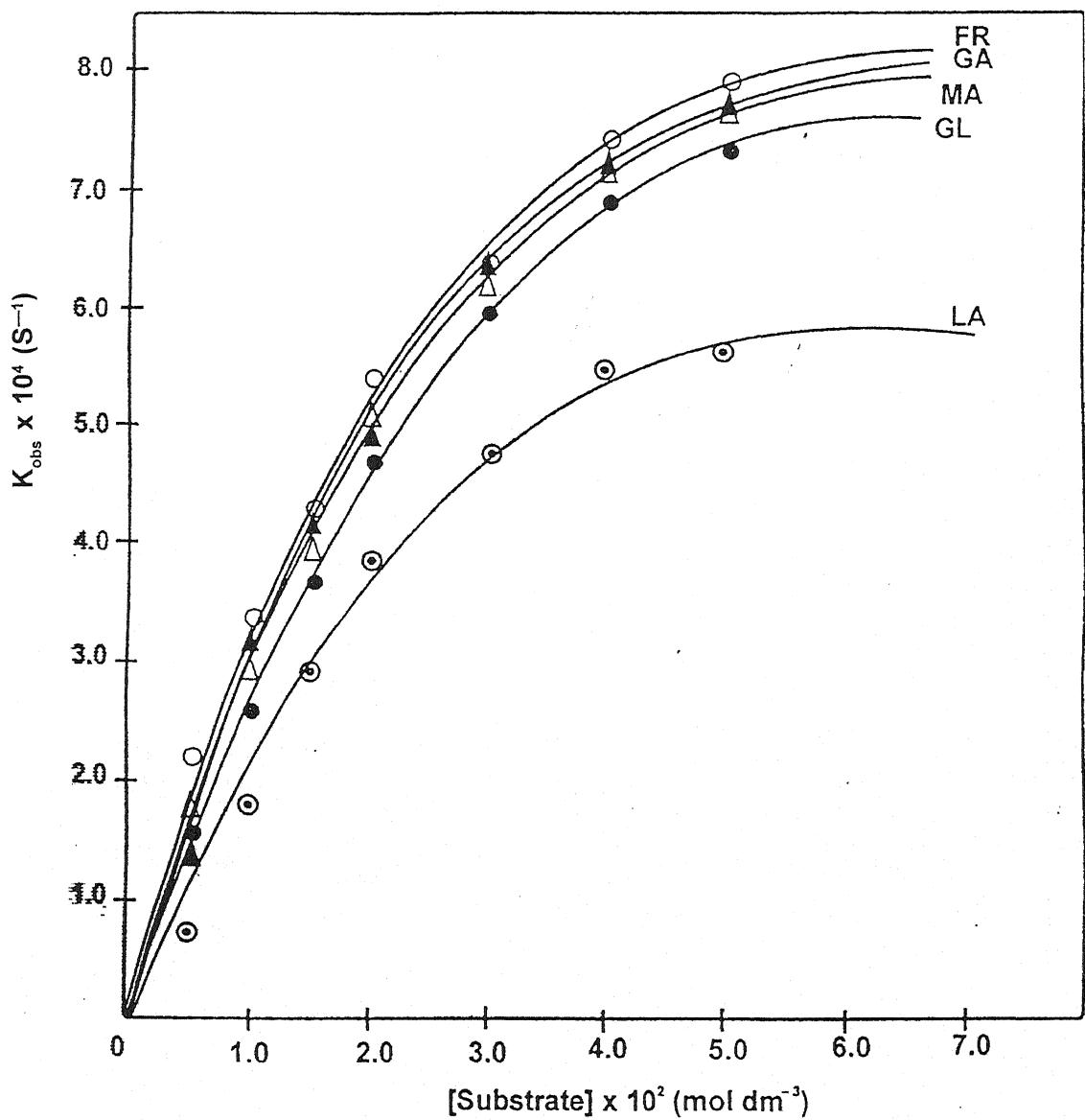


Fig. III D-6 : Pseudo of ( $k_{obs}$ ) Vs [S] at 40°C

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{OH}^-] = 0.10$  for A, B and C;

$0.20$  for D and E;  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ ,

Concentrations are in  $\text{mol dm}^{-3}$ .

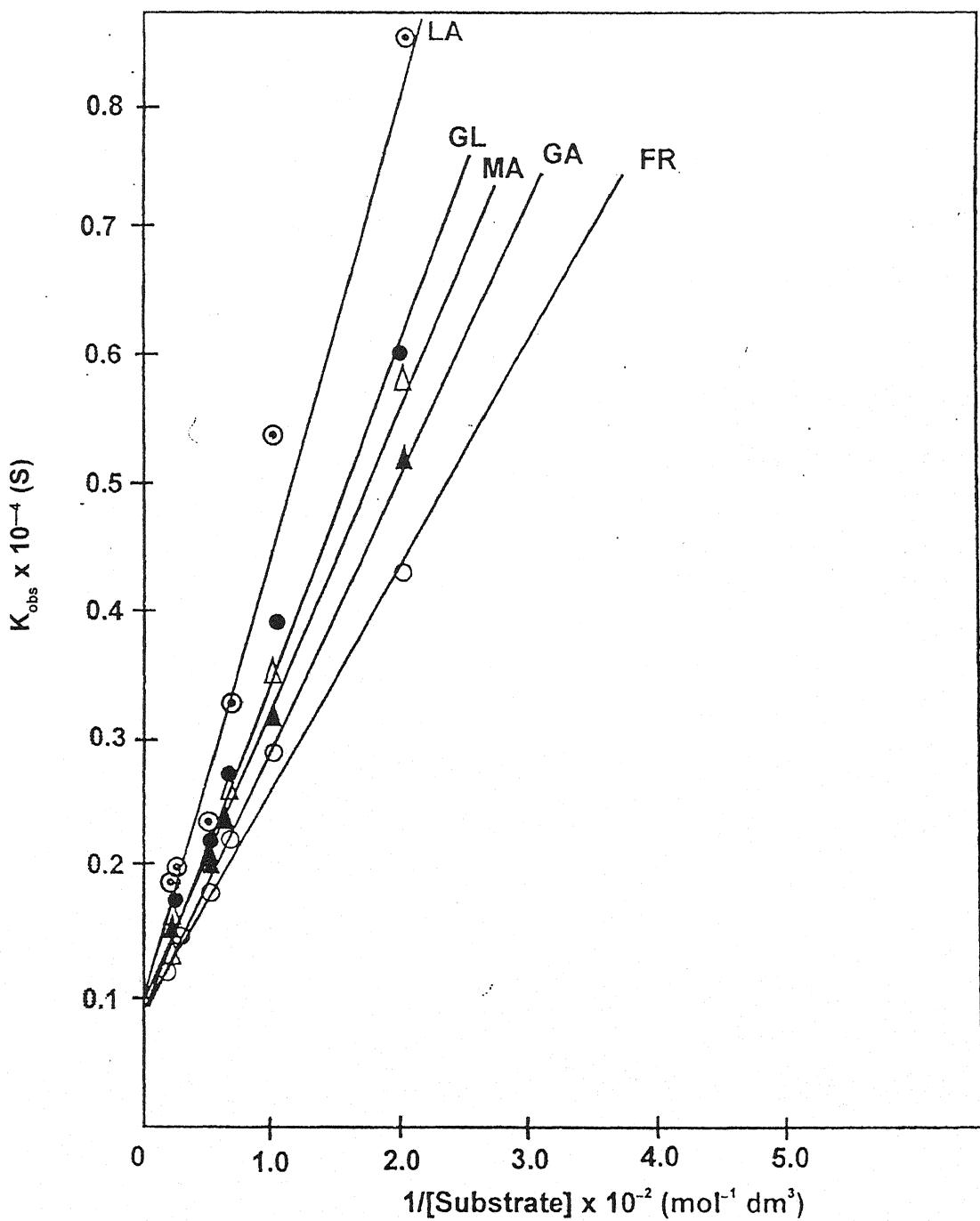


Fig. III D-6 : Pseudo of ( $k_{obs}$ ) Vs [S] at 40°C

$[IO_4^-] = 2.0 \times 10^{-3}$ ,  $[OH^-] = 0.10$  for A, B and C;

0.20 for D and E;  $RuCl_3] = 3.0 \times 10^{-4}$ ,

Concentrations are in mol dm<sup>-3</sup>.

The observed rate constant ( $k_{\text{obs}}$ ) evaluated from the slopes of the linear plots between  $\log (a - x)$  versus time (Figures III E-1 to III E-5) are summarised in Table – III E-1.

It is observed that on increasing  $[\text{OH}^-]$  at fixed ionic strength, the  $k_{\text{obs}}$  increases and a plot of  $(k_{\text{obs}})$  versus  $[\text{OH}^-]$  showed a deviation from linearity (Figures III E-6). However, a plot of  $(1/k_{\text{obs}})$  versus  $(1/[\text{OH}^-])$  was linear with a positive intercept (Figure III E-7). Therefore, it is clear, that order of reaction in  $\text{OH}^-$  decreases from unity to zero at higher  $[\text{OH}^-]$ . The results are similar to that of substrate effect on the rate.

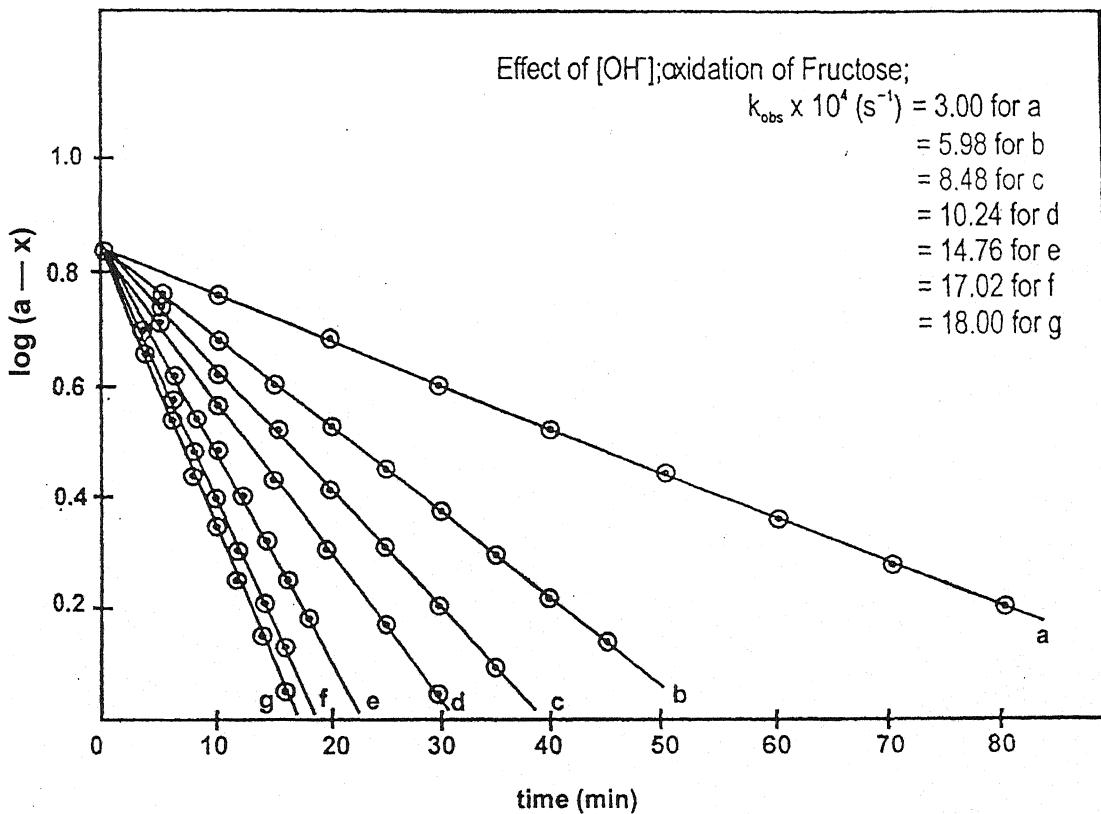


Fig. III E -1 : Pseudo- first order plots at 40°C

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{S}] = 0.2 \times 10^{-2}$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ ,  
 $[\text{OH}^-] = 0.5, 1.0, 1.5, 2.0, 3.0, 4.0$  and  $5.0 \times 10^{-1}$ ,  
 in a, b, c, d, e, f and g respectively,  $\mu = 4.0$   
 Concentrations are in mol  $\text{dm}^{-3}$ .

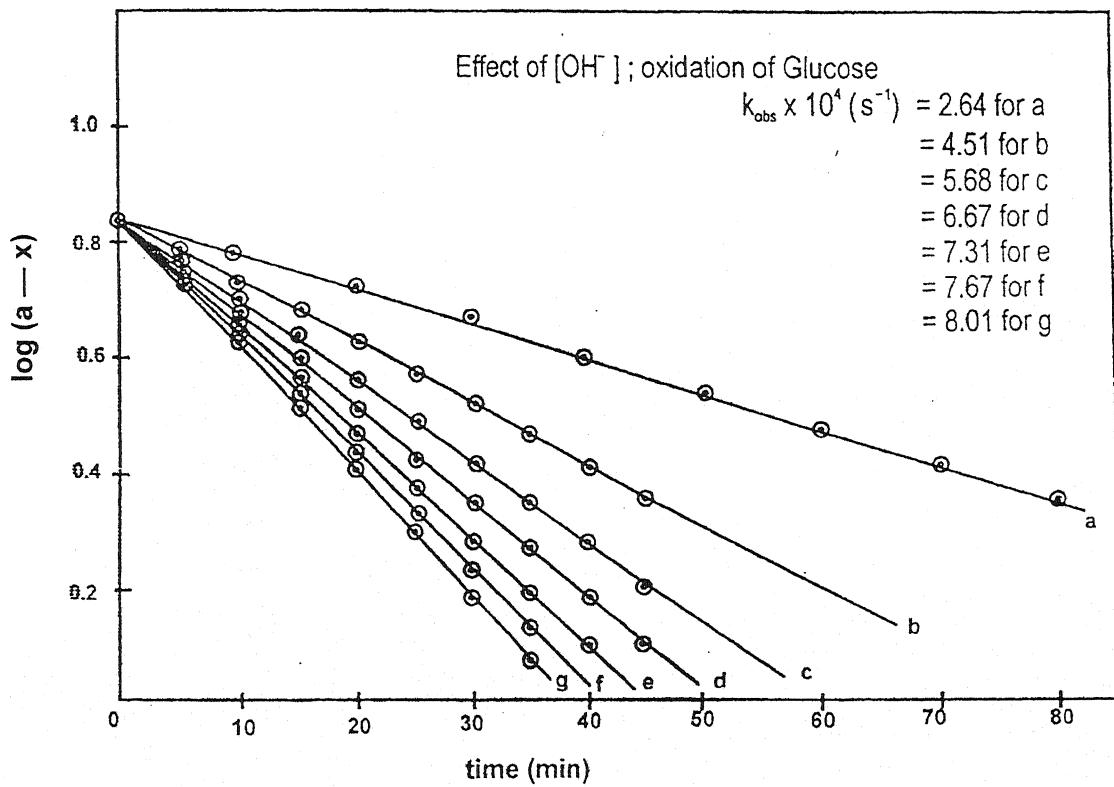


Fig. III E -2 : Pseudo- first order plots at  $40^\circ\text{C}$   
 $[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{S}] = 0.2 \times 10^{-2}$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ ,  
 $[\text{OH}^-] = 0.5, 1.0, 1.5, 2.0, 3.0, 4.0$  and  $5.0 \times 10^{-1}$ ,  
 in a, b, c, d, e, f and g respectively,  $\mu = 4.0$   
 Concentrations are in  $\text{mol dm}^{-3}$ .

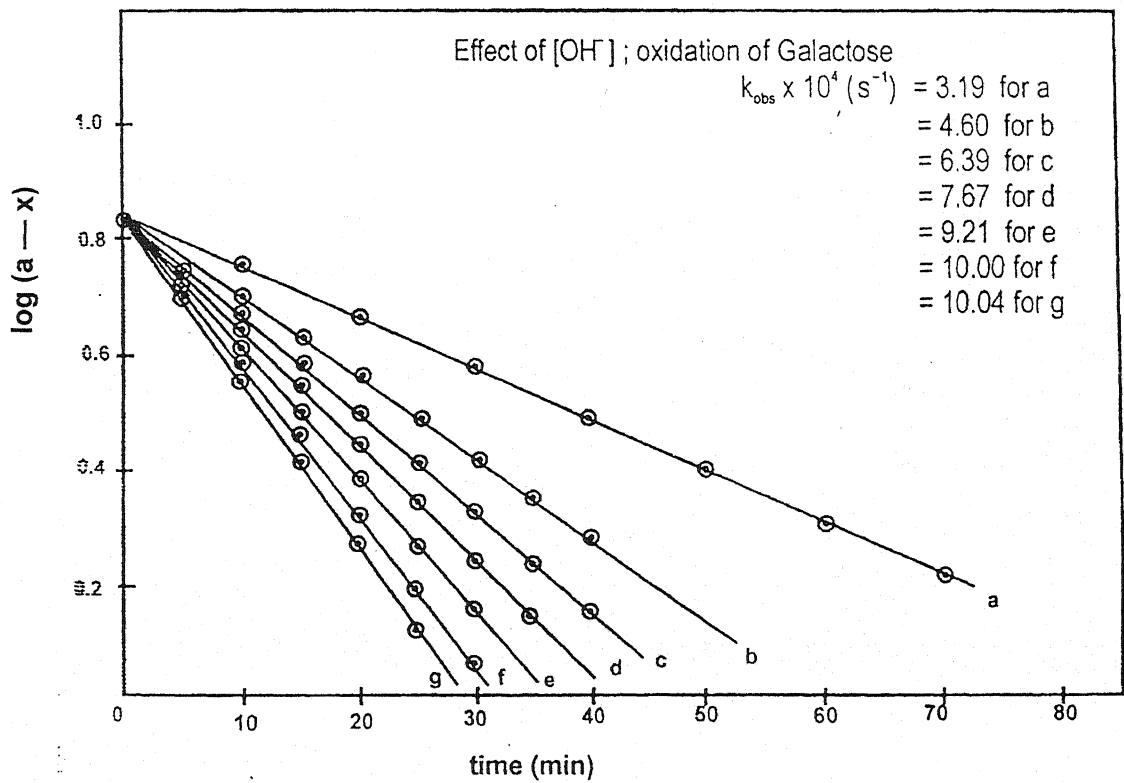


Fig. III E -3 : Pseudo- first order plots at 40°C

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{S}] = 0.2 \times 10^{-2}$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ ,  
 $[\text{OH}^-] = 0.5, 1.0, 1.5, 2.0, 3.0, 4.0$  and  $5.0 \times 10^{-1}$ ,  
 in a, b, c, d, e, f and g respectively,  $\mu = 4.0$   
 Concentrations are in mol  $\text{dm}^{-3}$ .

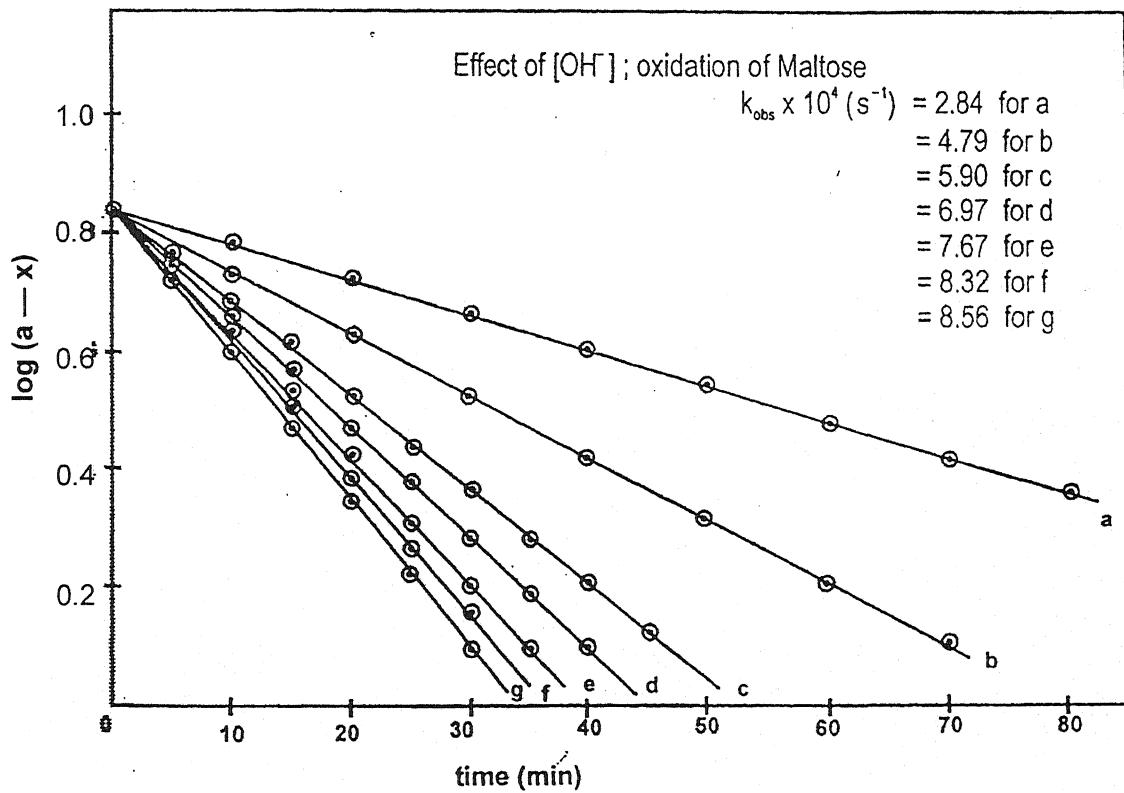


Fig. III E -4 : Pseudo- first order plots at  $40^\circ\text{C}$

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{S}] = 0.2 \times 10^{-2}$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ ,  
 $[\text{OH}^-] = 1.0, 2.0, 3.0, 4.0, 6.0, 8.0$  and  $10.0 \times 10^{-1}$ ,  
 in a, b, c, d, e, f and g respectively,  $\mu = 4.0$   
 Concentrations are in  $\text{mol dm}^{-3}$ .

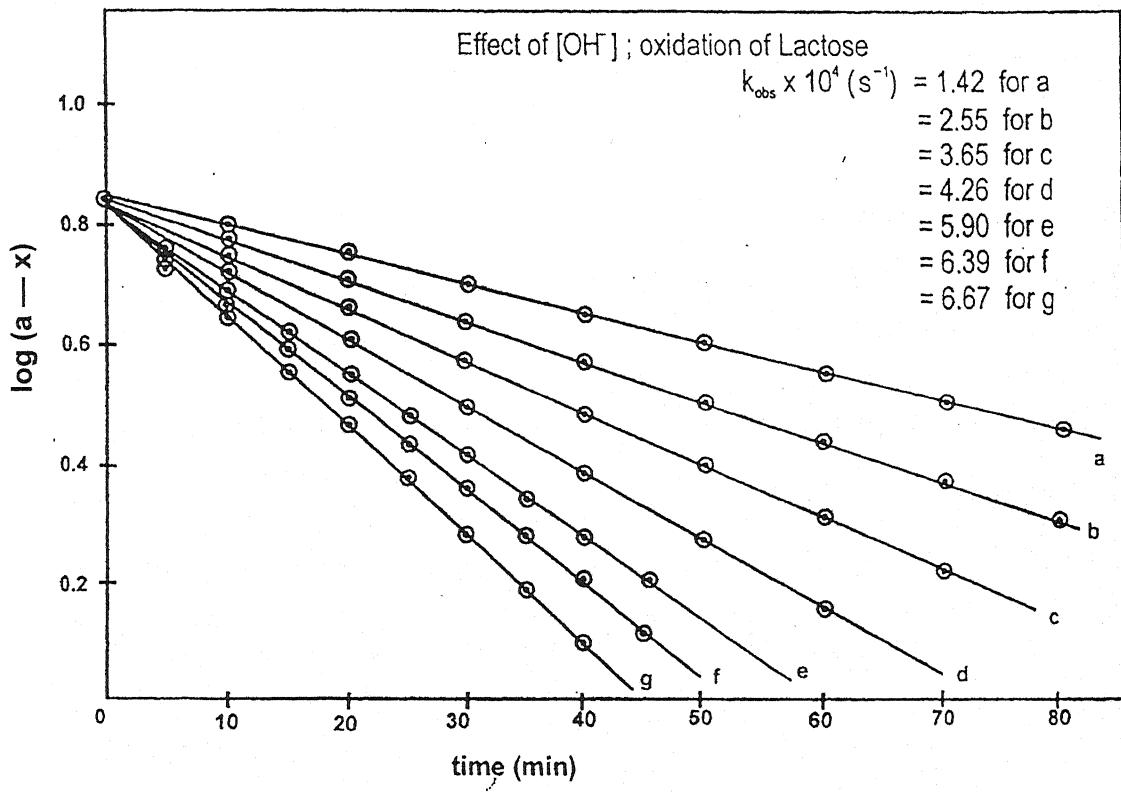


Fig. III E -4 : Pseudo- first order plots at  $40^\circ C$

$[IO_4^-] = 2.0 \times 10^{-3}$ ,  $[S] = 0.2 \times 10^{-2}$ ,  $[RuCl_3] = 3.0 \times 10^{-4}$ ,  
 $[OH^-] = 1.0, 2.0, 3.0, 4.0, 6.0, 8.0$  and  $10.0 \times 10^{-1}$ ,  
 in a, b, c, d, e, f and g respectively,  $\mu = 4.0$   
 Concentrations are in  $mol \text{ dm}^{-3}$ .

### **III F. Effect of $[RuCl_3]$ on the Rate of Oxidation:**

In order to investigate the effect of catalyst i.e. ruthenium trichloride, on the rate of reaction, the kinetics of oxidation of all the reducing sugars under investigations were studied at several initial concentrations of ruthenium-trichloride, keeping the concentrations of all the other reactants at constant.

The amount of hypo required for titration of 5 ml. of the reaction mixture at different time intervals for various kinetic runs are presented in Table III-16 to III-20

The Pseudo-first order plots i.e.  $\log (a-x)$  versus time plots at different initial  $[RuCl_3]$  are represented graphically in Figures III F-1 to III F-5.

**Table - III E - 1 : Effect of  $[OH^-]$  on the rate constants at  $40^\circ C$**

$[IO_4^-] \times 10^2 \downarrow$	$FR(A) \downarrow$	$GL(B) \downarrow$	$GA(C) \downarrow$	$MA(D) \downarrow$	$LA(E) \downarrow$	$(k_{obs}) \times 10^4 (s^{-1})$
0.5	3.0	2.64	3.19	1.0	2.84	1.42
1.0	5.98	4.51	4.60	2.0	4.79	2.55
1.5	8.48	5.68	6.39	3.0	5.90	3.65
2.0	10.24	6.67	7.67	4.0	6.97	4.26
3.0	14.76	7.31	9.21	6.0	7.67	5.90
4.0	17.02	7.67	10.00	8.0	8.32	6.39
5.0	18.00	8.01	10.04	10.0	8.56	6.67

(6)

$[IO_4^-] = 2.0 \times 10^{-3}$ ; [Substrate] =  $2.0 \times 10^{-2}$ ;  $[RuCl_3] = 3.0 \times 10^{-4}$ ;  $\mu = 0.4$  for A, B and C; 0.8 for D and E;

The concentration of reactants are in mol  $Dm^{-3}$ .

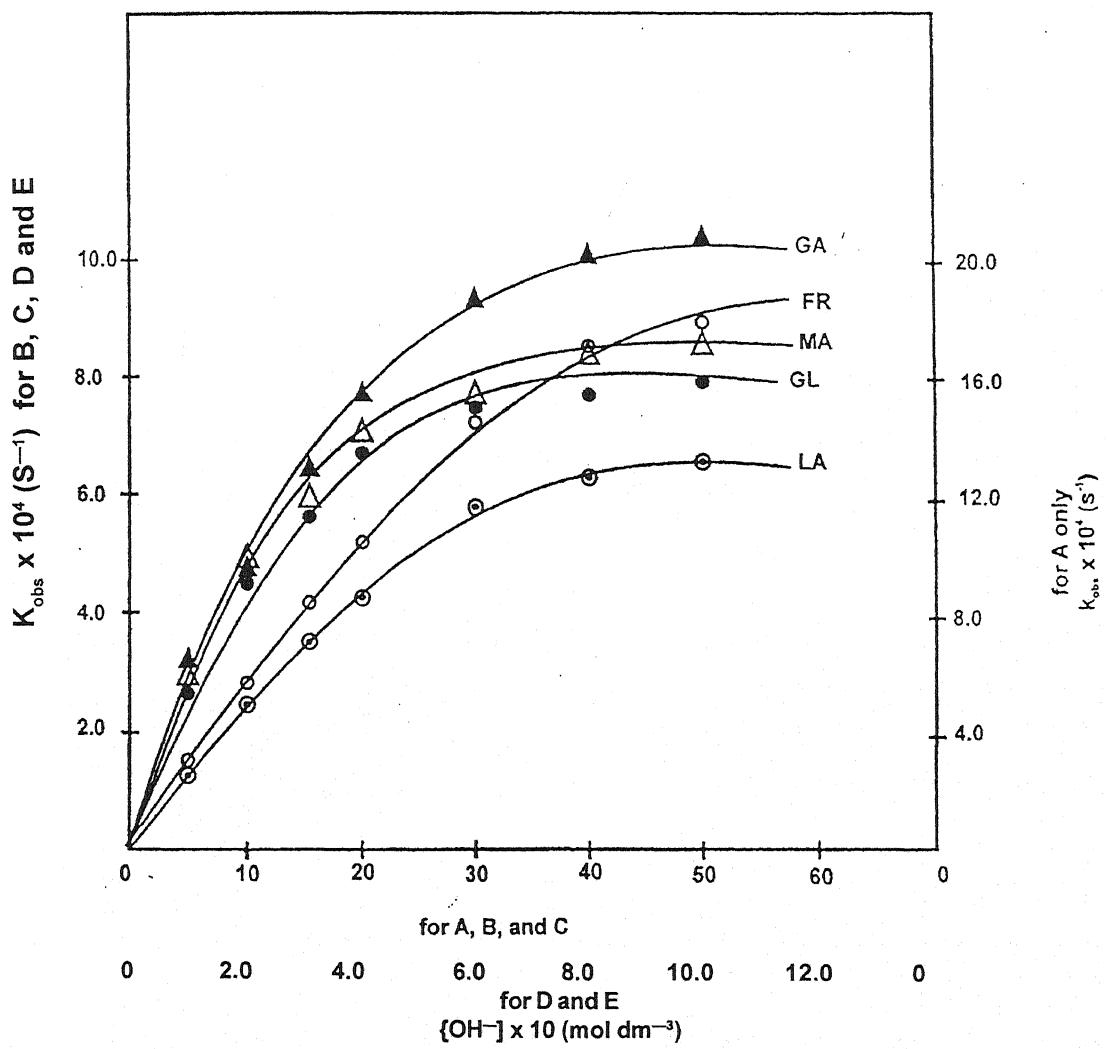


Fig. III E-6 : Pseudo of  $k_{\text{obs}}$  Vs  $[\text{OH}^-]$  at  $40^\circ\text{C}$

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{S}] = 2.0 \times 10^{-2}$

$[\text{RuCl}_3] = 3.0 \times 10^{-4}$ ,  $\mu = 0.4$  for A, B and C;  
0.8 for D and E

Concentrations are in  $\text{mol dm}^{-3}$ .

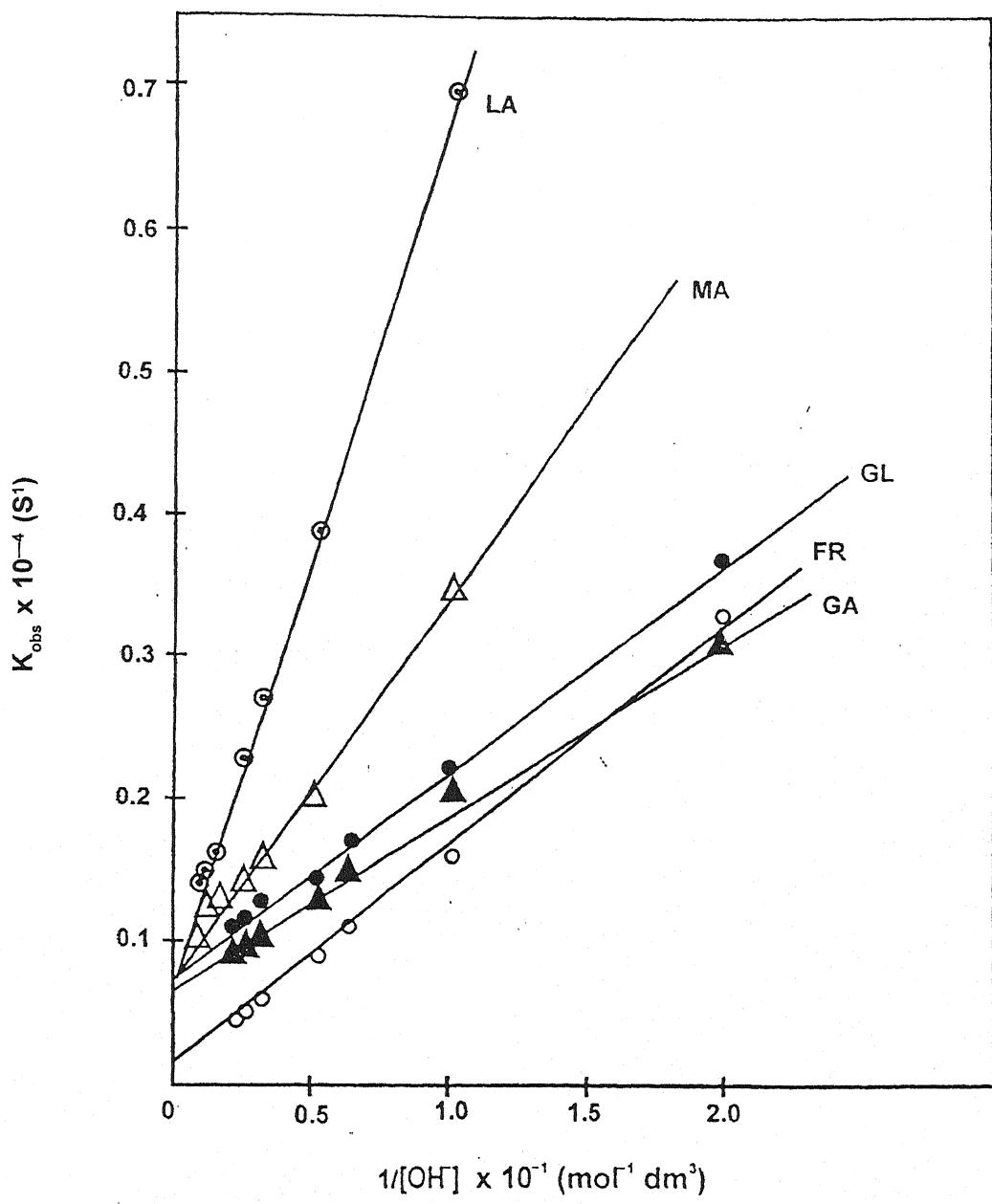


Fig. III E-6 : Pseudo of  $k_{obs}$  Vs  $[OH^-]$  at 40°C

$$[IO_4^-] = 2.0 \times 10^{-3}, [S] = 2.0 \times 10^{-2}$$

$$[RuCl_3] = 3.0 \times 10^{-4}, \mu = 0.4 \text{ for A, B and C;} \\ 0.8 \text{ for D and E}$$

Concentrations are in mol dm<sup>-3</sup>.

The pseudo-first order rate constant obtained from the slopes of  $\log (a-x)$  versus time plots (Figures III F-1) to III F-5) at various initial concentrations of  $(\text{RuCl}_3)$  are summarized in Table- III F-1. The rate constants ( $k_{\text{obs}}$ ) were also evaluated fro uncatalysed path i.e. when  $[\text{RuCl}_3] = 0$

The plot of ( $k_{\text{obs}}$ ) versus  $[\text{RuCl}_3]$  (Figure III F-6) was linear with an intercept suggesting that rate constant increases on increasing  $[\text{RuCl}_3]$  in case of each reducing sugar and also reveals that, rate is proportional to  $\{k' + k'' [\text{RuCl}_3]\}$  where  $k'$  and  $k''$  are rate constant for uncatalysed and catalysed path, respectively. The reactions were proceeded in absence of the catalyst. However, in absence of the catalyst, the reactions were found to be extremely slow. The observed rate constant for uncatalys path ( $k'$ ) i.e.  $k_{\text{obs}}$  at  $(\text{RuCl}_3] = 0$ , was matching with the value of intercept of the plot of ( $k_{\text{obs}}$ ) versus  $[\text{RuCl}_3]$  in case of each reducing sugar.

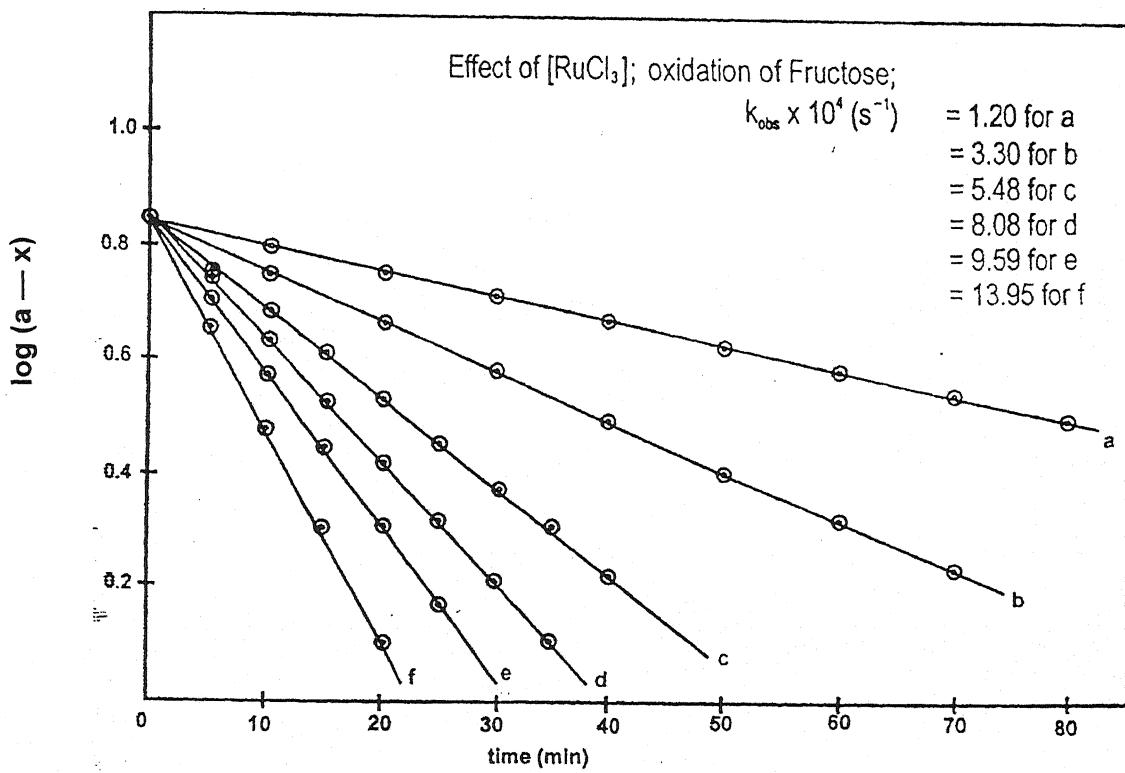


Fig. III F-1 : Pseudo- first order plots at  $40^\circ\text{C}$

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{S}] = 0.2 \times 10^{-2}$ ,  $[\text{OH}^-] = 1.0$  and

$[\text{RuCl}_3] = \text{Nil}, 1.5, 3.0, 4.5, 6.0$  and  $9.0 \times 10^{-4}$ ,

in a, b, c, d, e and f respectively,  $\mu = 4.0$

Concentrations are in  $\text{mol dm}^{-3}$ .

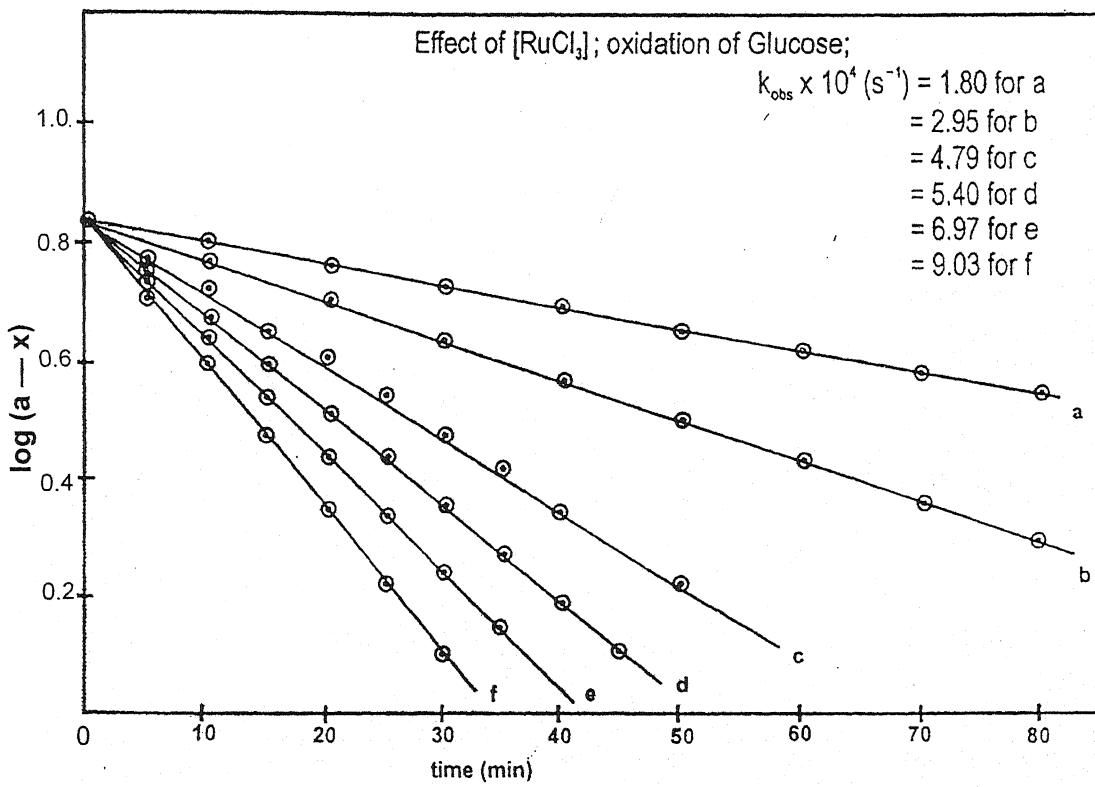


Fig. III F-2 : Pseudo- first order plots at  $40^\circ\text{C}$

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{S}] = 0.2 \times 10^{-2}$ ,  $[\text{OH}^-] = 1.0$  and  
 $[\text{RuCl}_3] = \text{Nil}, 1.5, 3.0, 4.5, 6.0$  and  $9.0 \times 10^{-4}$ ,  
 in a, b, c, d, e and f respectively,  $\mu = 4.0$   
 Concentrations are in  $\text{mol dm}^{-3}$ .

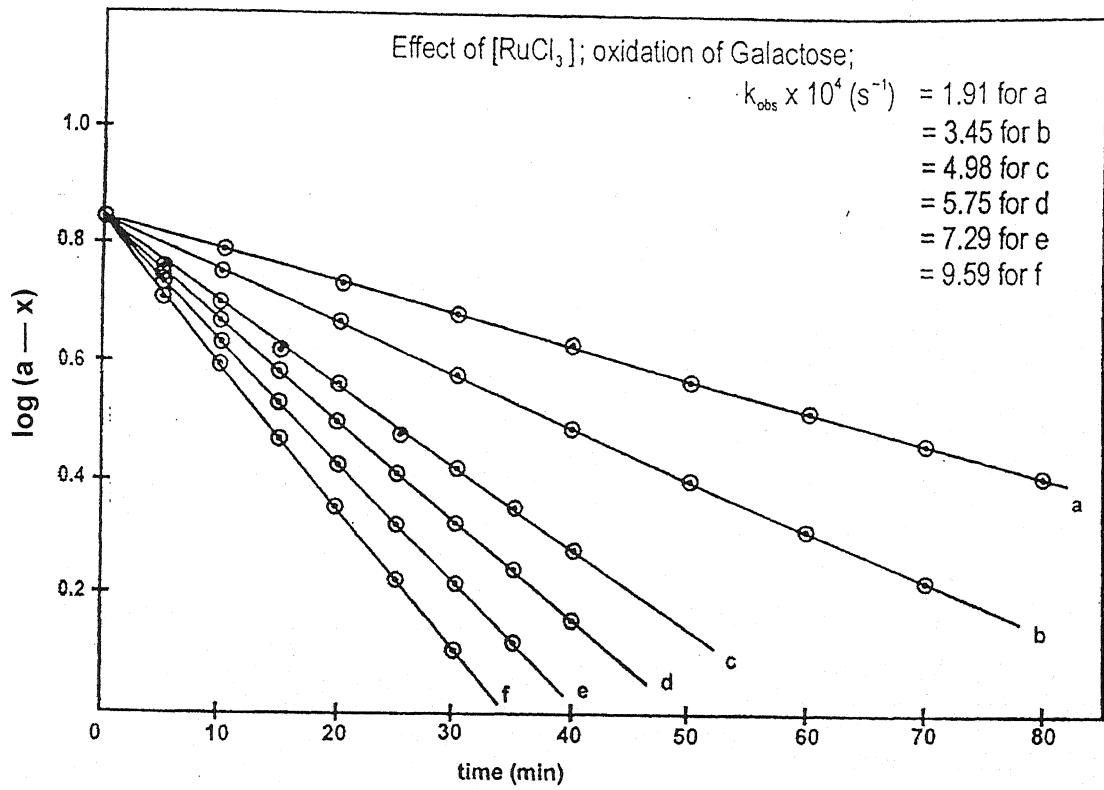


Fig. III F-3 : Pseudo- first order plots at  $40^\circ\text{C}$

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{S}] = 0.2 \times 10^{-2}$ ,  $[\text{OH}^-] = 1.0$  and  
 $[\text{RuCl}_3] = \text{Nil}, 1.5, 3.0, 4.5, 6.0$  and  $9.0 \times 10^{-4}$ ,  
 in a, b, c, d, e and f respectively,  $\mu = 4.0$   
 Concentrations are in  $\text{mol dm}^{-3}$ .

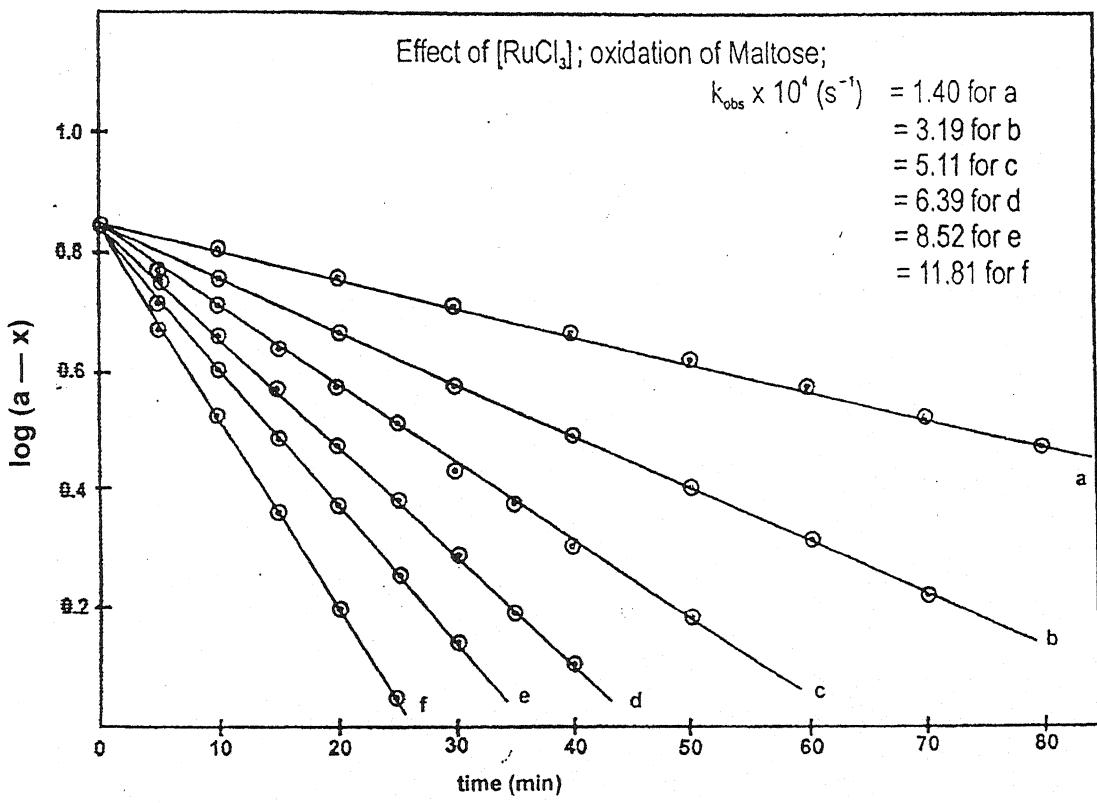


Fig. III F-4 : Pseudo- first order plots at 40°C

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{S}] = 0.2 \times 10^{-2}$ ,  $[\text{OH}^-] = 1.0$  and  
 $[\text{RuCl}_3] = \text{Nil}, 1.5, 3.0, 4.5, 6.0$  and  $9.0 \times 10^{-4}$ ,  
 in a, b, c, d, e and f respectively,  $\mu = 4.0$   
 Concentrations are in mol dm<sup>-3</sup>.

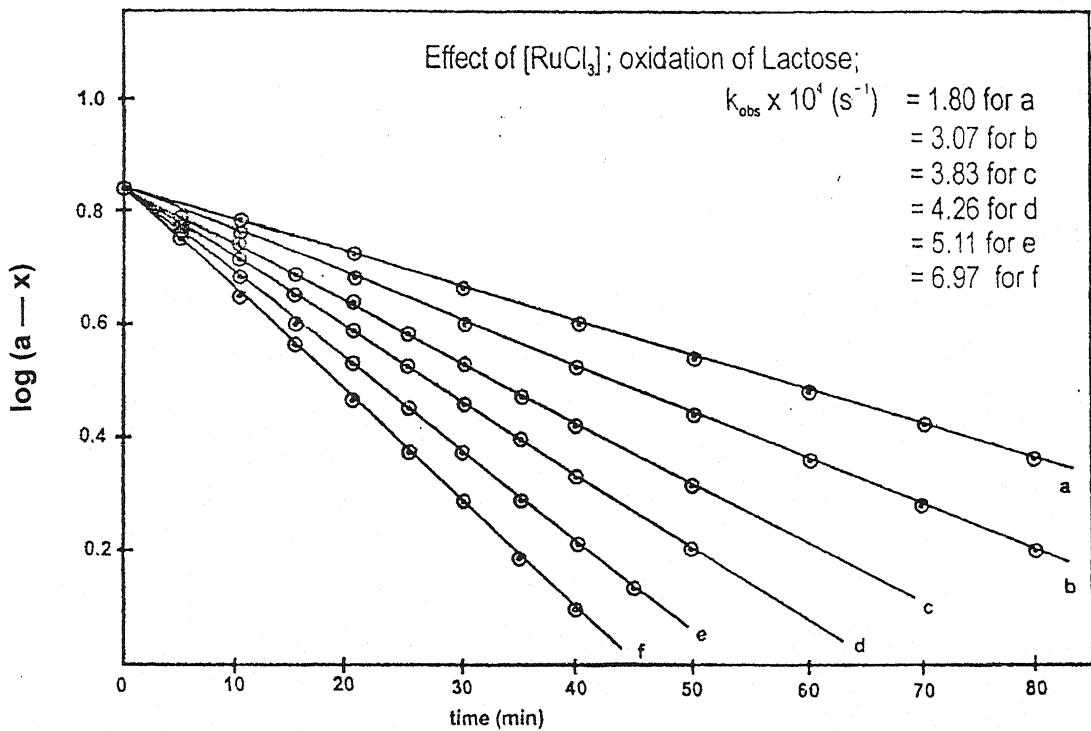


Fig. III F-5 : Pseudo- first order plots at  $40^\circ\text{C}$

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{S}] = 0.2 \times 10^{-2}$ ,  $[\text{OH}^-] = 1.0$  and

$[\text{RuCl}_3] = \text{Nil}, 1.5, 3.0, 4.5, 6.0$  and  $9.0 \times 10^{-4}$ ,

in a, b, c, d, e and f respectively,  $\mu = 4.0$

Concentrations are in  $\text{mol dm}^{-3}$ .

### **III G. Effect of temperature on the Rate of Oxidation:**

To investigate the effect of temperature on the reaction rate and to determine activation parameters, the kinetic runs were made at four different temperatures viz. 35, 40, 45 and 50°C. The concentrations of all the reactants were kept constant as mentioned in corresponding Tables III-21 to III-25.

The volume of hypo required for titration of 5 ml of reaction mixture at different time intervals for each kinetic run was determined. With the help of these data, the  $\log (a-x)$  versus time plots i.e. pseudo-first order plots in metaperiodate have been obtained. The results are represented in Figures III G-1 to III -G-5.

**Table - III F-1 : Effect of  $[\text{RuCl}_3]$  on the rate constants at  $40^\circ\text{C}$**

$[\text{RuCl}_3] \times 10^4 \downarrow$	$\text{FR}(\text{A}) \downarrow$	$\text{GL}(\text{B}) \downarrow$	$(\text{k}_{\text{obs}}) \times 10^4 \text{ (s}^{-1}\text{)}$	$\text{GA}(\text{C}) \downarrow$	$\text{MA}(\text{D}) \downarrow$	$\text{LA}(\text{E}) \downarrow$
Nil	1.20	1.80	1.91	1.40	1.80	
1.5	3.30	2.95	3.45	3.19	3.07	
3.0	5.48	4.79	4.98	5.11	3.83	
4.5	8.08	5.40	5.75	6.39	4.26	
6.0	9.59	6.97	7.29	8.52	5.11	
9.0	13.95	9.03	9.59	11.81	6.97	

(76)

$[\text{O}_4^-] = 2.0 \times 10^{-3}$ ; [Substrate] =  $2.0 \times 10^{-2}$ ;  $(\text{OH}^-) = 0.10$  for A, B and C; 0.20 for D and E;

The concentration of reactants are in  $\text{mol Dm}^{-3}$ .

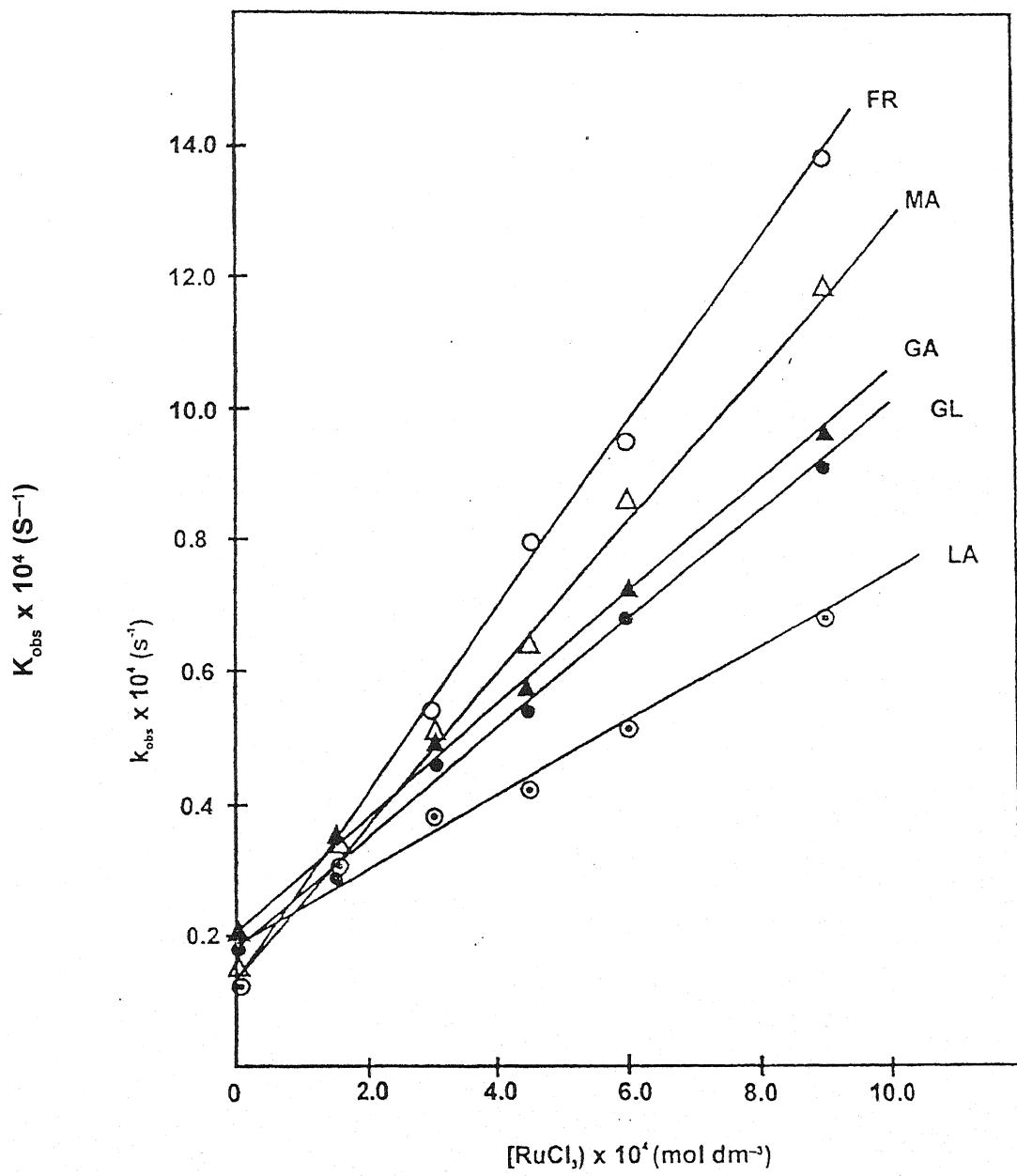


Fig. III F-6 : Pseudo of  $k_{obs}$  Vs  $[\text{RuCl}_3]$  at 40°C  
 $[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{S}] = 2.0 \times 10^{-2}$   
 $[\text{OH}^-] = 0.1$  for A, B and C; 0.2 for D and E  
Concentrations are in mol dm<sup>-3</sup>.

The pseudo – first order rate constant ( $K_{obs}$ ) obtained from  $\log(a-x)$  versus time plots at different temperatures in case of various reducing sugars are summarized in Table – III G.1.

It is observed from the Table III G – 1 that ( $K_{obs}$ ) increases on increasing temperature with a temperature coefficient = 2.12, 2.96, 2.42, 2.86, 2.63 in case of fructose, glucose, galactose, maltose and lactose, respectively.

In order to determine the energy of activation of the reaction ( $E_{act}$ ), the Arrhenius plot i.e. plot of  $\log(k_{obs})$  versus  $1/T$  was plotted in each case. (Figure – III G-6). From the slope of the Arrhenius plot the value of  $E_{act}$  ( $E_{act} = 2.303 \times R \times \text{slope}$ ) has been evaluated.

The other activation parameters have also been evaluated using the following relations:

$$\Delta H^\# = E_{act} - RT \quad (i)$$

$$K_{obs} = \frac{K_b T}{h} e^{\Delta S^\# / R} e^{-E_{act} / RT} \quad (ii)$$

$$\Delta G^\# = \Delta H^\# - T \Delta S^\# \quad (iii)$$

Where , R = Gas constant

h= Planck's Constant

$k_b$  = Boltzmann constant

$\Delta S^\#$  = Entropy change

$\Delta H^\#$  = Enthalpy change

$\Delta G^\#$  = Gibb's free energy change

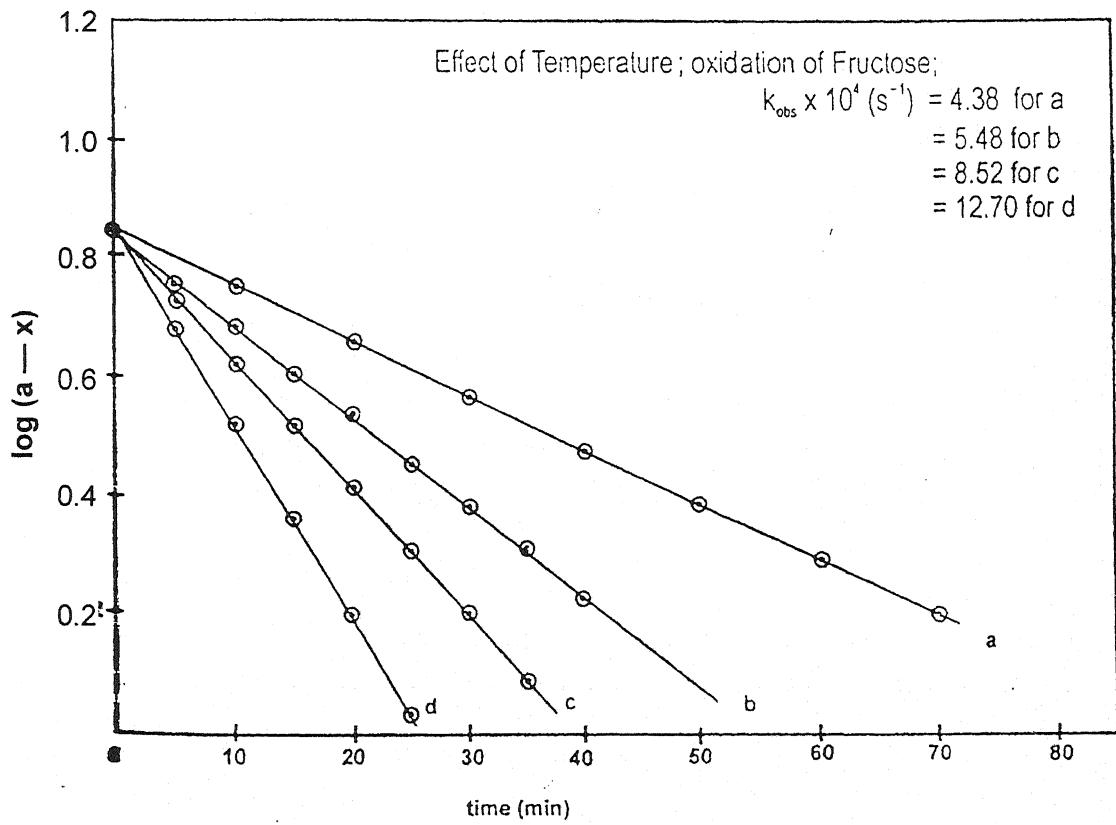


Fig. III G-1 : Pseudo first order plots

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{OH}^-] = 1.0$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$

Nil, 1.5, 3.0, 4.5, 6.0 and  $9.0 \times 10^{-4}$ ,

$[\text{S}] = 0.2 \times 10^{-2}$ , and temp. = 35, 40, 45 and  $50^\circ\text{C}$

in a, b, c, and d respectively

Concentrations are in  $\text{mol dm}^{-3}$ .

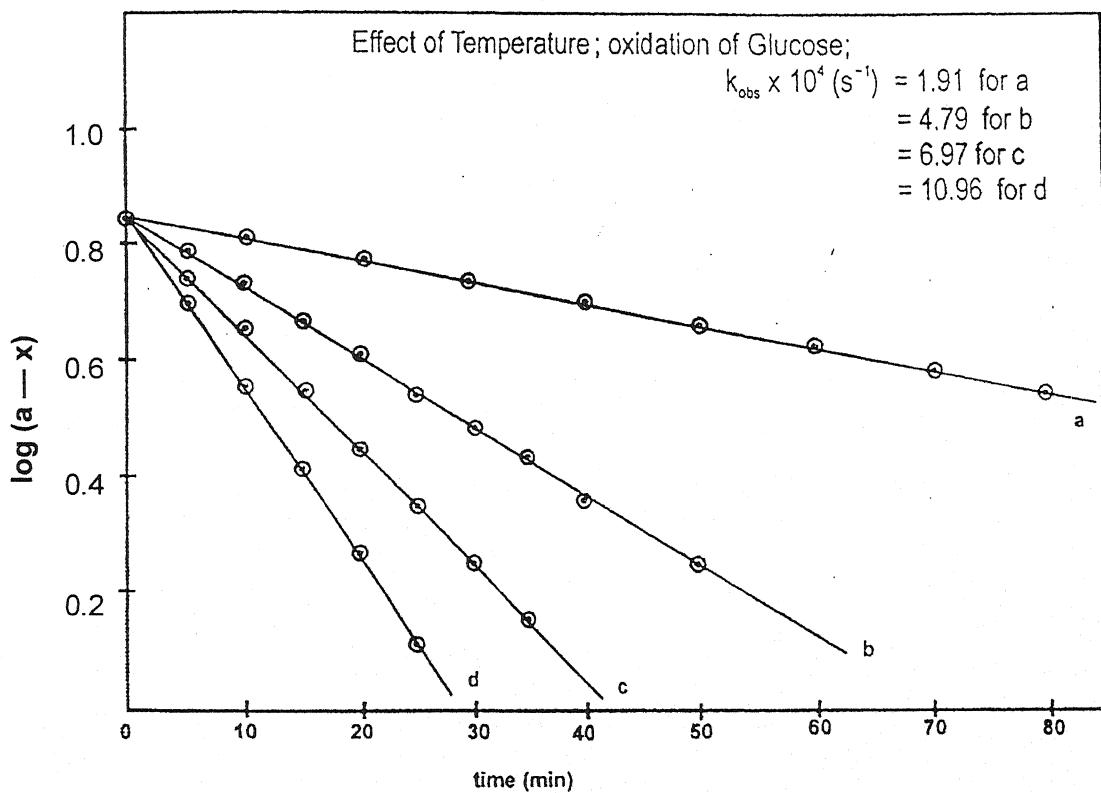


Fig. III G-2 : Pseudo first order plots

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{OH}^-] = 1.0$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$

Nil, 1.5, 3.0, 4.5, 6.0 and  $9.0 \times 10^{-4}$ ,

$[\text{S}] = 0.2 \times 10^{-2}$ , and temp. = 35, 40, 45 and  $50^\circ\text{C}$

in a, b, c, and d respectively

Concentrations are in  $\text{mol dm}^{-3}$ .

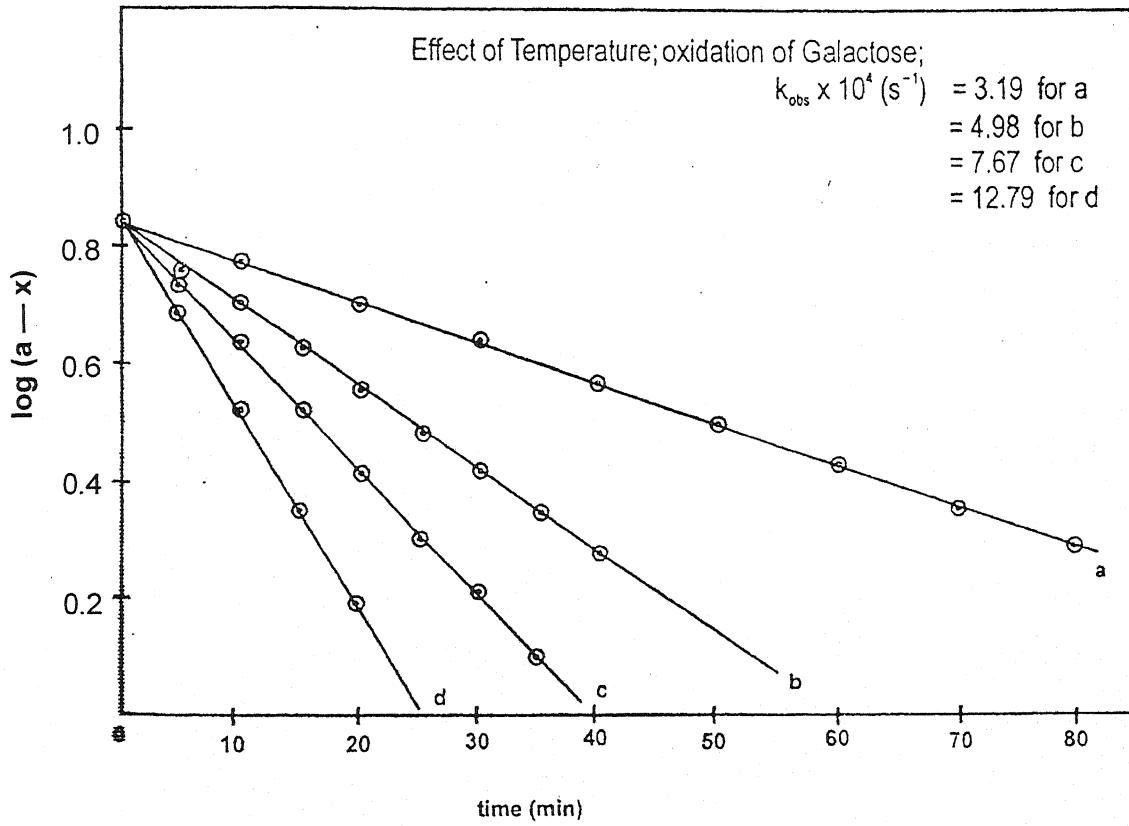


Fig. III G-3 : Pseudo first order plots

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{OH}^-] = 1.0$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$

Nil, 1.5, 3.0, 4.5, 6.0 and  $9.0 \times 10^{-4}$ ,

$[\text{S}] = 0.2 \times 10^{-2}$ , and temp. = 35, 40, 45 and  $50^\circ\text{C}$

in a, b, c, and d respectively

Concentrations are in mol dm<sup>-3</sup>.

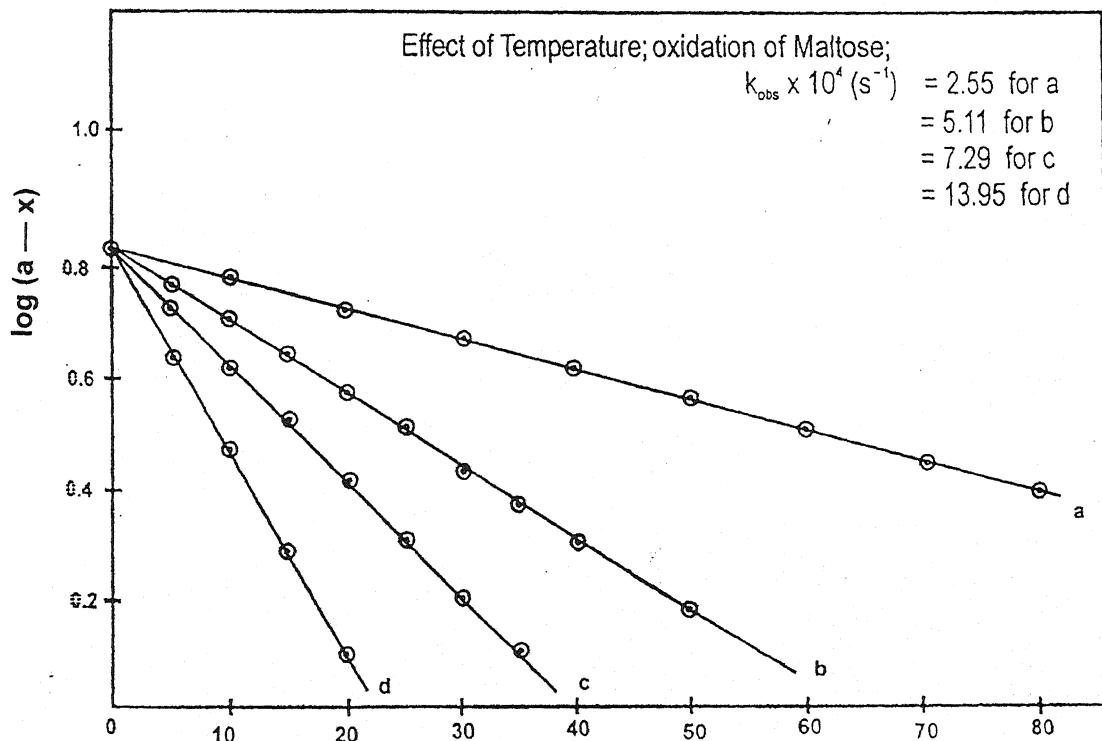


Fig. III G-4 : Pseudo first order plots

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{OH}^-] = 1.0$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$

Nil, 1.5, 3.0, 4.5, 6.0 and  $9.0 \times 10^{-4}$ ,

$[\text{S}] = 0.2 \times 10^{-2}$ , and temp. = 35, 40, 45 and 50°C

in a, b, c, and d respectively

Concentrations are in mol dm<sup>-3</sup>.

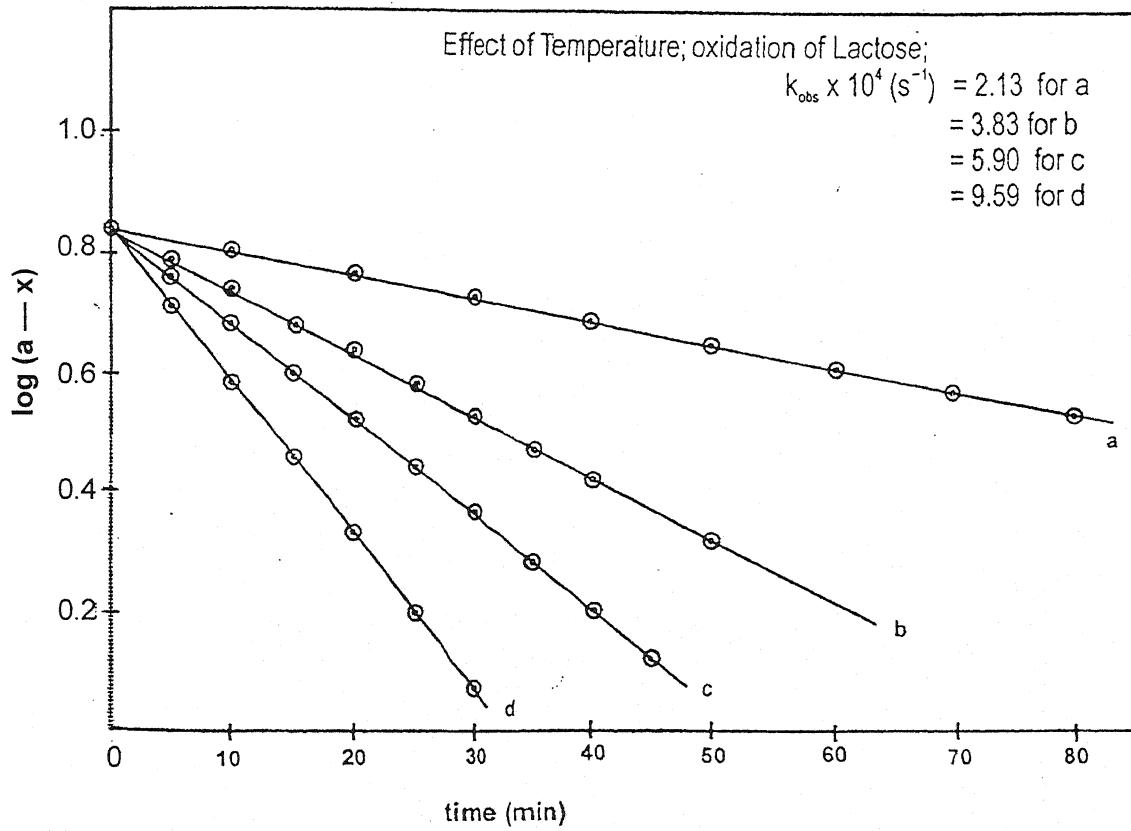


Fig. III G-5 : Pseudo first order plots

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{OH}^-] = 1.0$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$

Nil, 1.5, 3.0, 4.5, 6.0 and  $9.0 \times 10^{-4}$ ,

$[\text{S}] = 0.2 \times 10^{-2}$ , and temp. = 35, 40, 45 and  $50^\circ\text{C}$

in a, b, c, and d respectively

Concentrations are in  $\text{mol dm}^{-3}$ .

The activation parameters are summarized in Table III-G-2. It is observed from Table III G-2 that  $\Delta G^\#$  is almost same ( $\sim 94.34^\circ 1.0 \text{ kJ mol}^{-1}$ ) for all reducing sugars suggesting that the oxidation of reducing sugars follow almost a common mechanism.

### III H. Influence of Ionic Strength:

The effect of ionic strength on the rate of oxidation of each reducing sugars has also been investigated by adding different amount of sodium perchlorate ( $\text{NaClO}_4$ ) in the reaction mixture. The reactants concentrations were kept constant as mentioned in Table-III- 26 to III-30 in which result of effect of  $\text{NaClO}_4$  are presented.

The observed pseudo-first order rate constants is metaperiodate ( $k_{\text{obs}}$ ) at different initial concentrations of sodium perchlorate obtained from the slopes of straight lines plotted between  $\log (a-x)$  versus times are summarized in Table – III H-1.

**Table - III G-1 : Effect of Temperature on the rate constants.**

$^{\circ}\text{C}$	Tempearture $\downarrow$	$\xrightarrow{\text{FR (A) } \downarrow}$	$\xrightarrow{\text{GL (B) } \downarrow}$	$\xleftarrow{\text{GA (C) } \downarrow}$	$\xleftarrow{\text{MA (D) } \downarrow}$	$\xleftarrow{\text{LA (E) } \downarrow}$
35		4.38	1.91	3.19	2.55	2.13
40		5.48	4.79	4.98	5.11	3.83
45		8.52	6.97	7.29	7.67	5.90
50		12.70	10.96	12.79	13.95	9.59
	(Temp coefficient) <sub>average</sub>	2.12	2.96	2.42	2.86	2.63

(86)

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ , [Substrate] =  $2.0 \times 10^{-2}$ ;  $(\text{OH}^-) = 0.10$  for A, B and C; 0.20 for D and E;  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ .

The concentration of reactants are in mol  $\text{Dm}^{-3}$ .

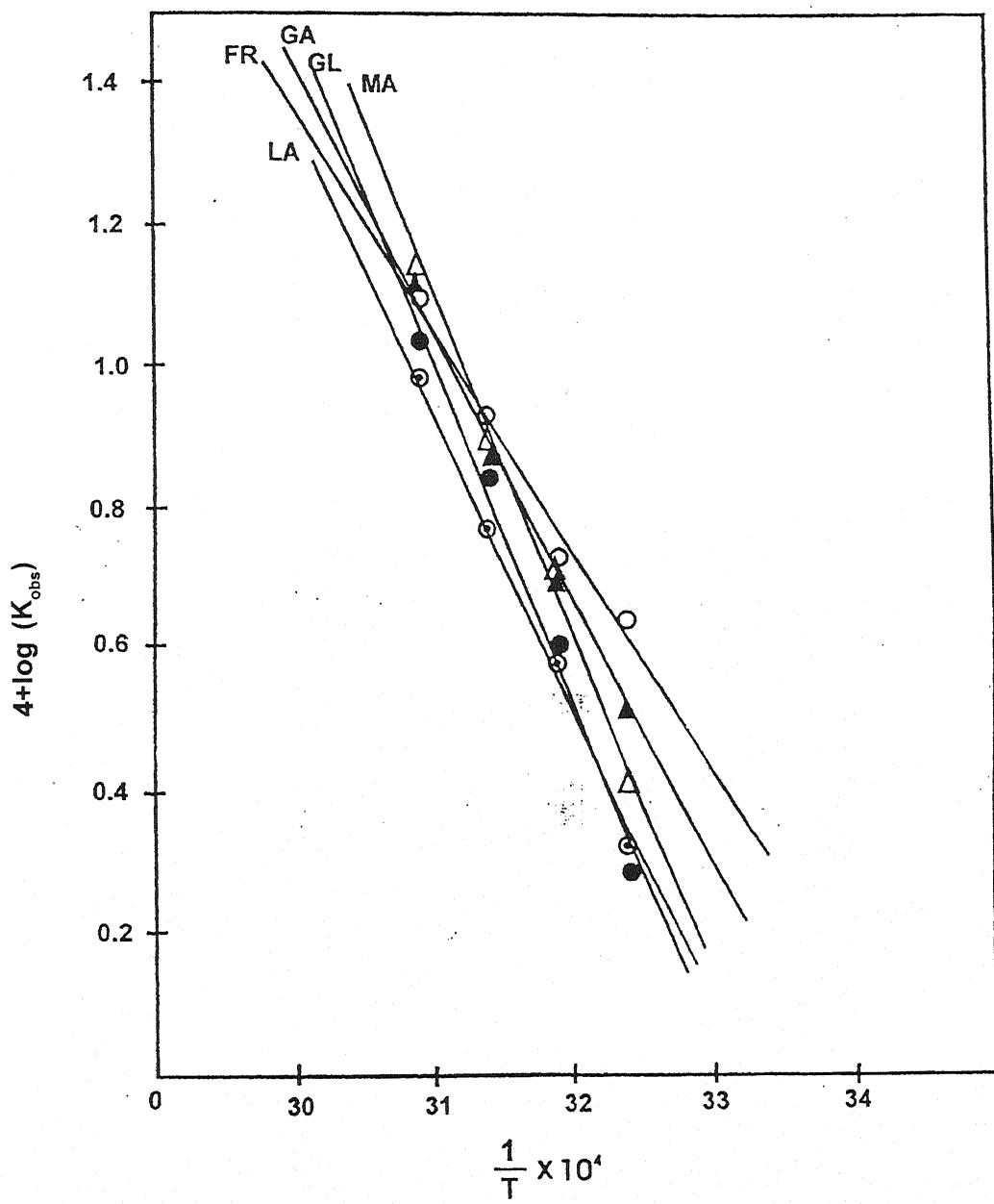


Fig. III G-6 : Arrhenius plots of  $\log(k_{\text{obs}})$  Vs  $1/T$

$$[\text{IO}_4^-] = 2.0 \times 10^{-3}, [\text{S}] = 2.0 \times 10^{-2}$$

$$[\text{OH}^-] = 0.10 \text{ for A, B and C; } 0.20 \text{ for D and E}$$

$$[\text{RuCl}_3] = 3.0 \times 10^{-4}$$

Concentrations are in mol dm<sup>-3</sup>.

**Table - III G-2 : Activation parameters for the oxidation of reducing sugars in presence of  $\text{RuCl}_3$ .**

Substrate $\downarrow$	$E_{\text{act}} \downarrow$ (KJ mol $^{-1}$ )	$\log A \downarrow$	$\Delta H^\# \downarrow$ (KJ mol $^{-1}$ )	$\Delta S^\# \downarrow$ (KJ mol $^{-1}$ )	$\Delta G^\# \downarrow$ (KJ mol $^{-1}$ )
A, Fructose	58.80 $\pm$ 0.50	6.58 $\pm$ 0.02	56.17 $\pm$ 0.50	-119.17 $\pm$ 1.0	93.77 $\pm$ 1.0
B, Glucose	76.50 $\pm$ 0.50	9.35 $\pm$ 0.02	73.84 $\pm$ 0.50	-66.09 $\pm$ 0.50	94.72 $\pm$ 1.0
C, Galactose	63.79 $\pm$ 0.50	7.35 $\pm$ 0.02	61.17 $\pm$ 0.50	-104.44 $\pm$ 0.50	94.22 $\pm$ 1.0
D, Maltose	69.59 $\pm$ 0.50	8.30 $\pm$ 0.02	66.96 $\pm$ 0.50	-86.22 $\pm$ 1.0	94.16 $\pm$ 1.0
E, Lactose	85.05 $\pm$ 0.50	10.75 $\pm$ 0.03	82.42 $\pm$ 0.50	-39.45 $\pm$ 0.50	94.87 $\pm$ 1.0

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ; [Substrate] =  $2.0 \times 10^{-2}$ ;  $(\text{OH}^-) = 0.10$  for A, B and C; 0.20 for D and E;  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ .

The concentration of reactants are in mol Dm $^{-3}$ .

It is evident from Table III H-1 that an addition of sodium perchlorate ( $\text{NaClO}_4$ ) upto 0.2 M for fructose, glucose, galactose and 0.4 M for maltose and lactose) in the reaction mixture resulted an insignificant effect of the ionic strength on the observed pseudo-first order rate constant. Therefore, it may be concluded that at least one neutral species in involved (as one of the reactant) in the rate determining step of the mechanism.

**Table - III H - 1 : Effect of addition of [Sodium perchlorate] on the rate constants at 40°C**

[Sodium perchlorate] $\downarrow$	FR (A) $\downarrow$	GL (B) $\downarrow$	GA (C) $\downarrow$	[Sodium perchlorate] $\downarrow$	$(k_{obs}) \times 10^4 \text{ (s}^{-1}\text{)}$
Nil	5.48	4.98	Nil	5.11	3.83
5.0	5.48	4.98	4.98	10	5.11
10.0	5.94	4.98	5.18	20	5.56
15.0	6.14	5.37	5.18	30	5.75
20.0	6.14	5.56	5.37	40	5.94

(90)

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ , [Substrate] =  $2.0 \times 10^{-2}$ ,  $(\text{OH}^-) = 0.10$  for A, B and C; 0.20 for D and E;

$[\text{RuCl}_3] = 3.0 \times 10^{-4}$ .

The concentration of reactants are in mol  $\text{Dm}^{-3}$ .

### III. I. Evidence for complex Formation:

The ability of platinum group metal- ions to form complexes with organic substances in well reported in the literature 69-71. Spectrophotometric evidence for the formation of ruthenium (III) complex of metaperiodate and reducing sugars has been obtained in alkaline medium. All the studies have been made on spectronic - 20 spectrophotometer (MILTON ROY & COMP.)

It was observed that ruthenium (III) chloride in the present of NaOH and sodium metaperiodate absorbs maximum at 390 nm. The absorbance of sodium metaperiodate at 390 nm was negligible. A series of solutions were prepared containing a fixed amount of  $\text{RuCl}_3$  ( $3.80 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ), NaOH ( $0.1$  mol  $\text{dm}^{-3}$ ) and varying amounts of sodium metaperiodate. The absorbance of these solutions were measured at 390 nm at room temperature. The absorbance at different  $[\text{IO}_4^-]$  are recorded in Table – III I – 1. The plot of (absorbance) versus  $[\text{IO}_4^-]$  390 nm is represented in Figure. III I -1 (a). It is observed from the Figure (III I - 1a) that the absorbance of mixture decreases linearly until the ratio of  $[\text{Ru}^{\text{III}}]/[\text{IO}_4^-]$  nearly becomes unity, after that the absorbance of the mixtures slightly increases. The results indicate the formation of 1:1 complex between ruthenium (III) and  $\text{IO}_4^-$  that is the  $[\text{Ru}^{\text{III}}-\text{IO}_4^-]$  complex.

The possibility of the formation of complex between ruthenium (III) and reducing sugars was also tested in the similar manner by replacing sodium metaperiodate by reducing sugar in above solutions. No complex formation was observed at room temperature

(there was no change in absorbance.) However, when these solutions were heated at  $\sim 60^{\circ}\text{C}$  for about 15 minutes, allowed to cool at room temperature and then the absorbance were obtained at 390 nm, a change in absorbance of the solutions was observed. The results are given in Table-III I-1, and represented graphically in form of plot between (Absorbance) and [Reducing sugar] [Figure. III I-1 (b)]. The formation of 1:1 complex between ruthenium (III) and reducing sugar is also indicated from Figure. III I-1 (b). However, the complex between ruthenium (III) and reducing sugar under the similar conditions is observed only at high temperature ( $\sim 60^{\circ}\text{C}$ ) while that between ruthenium (III) and  $\text{IO}_4^-$  has been observed at low temperature ( $\sim 35^{\circ}\text{C}$ ). The formation of 1:1 complex between ruthenium (III) and various oxidants i.e.  $\{\text{RU}^{\text{III}}-\text{Bromide ion}\}$  Complex <sup>72</sup> and  $\{\text{Ru}^{\text{III}}-\text{IO}_4^-\}$ <sup>73-74</sup> complex is also reported in the literature.

### III. J. Kinetic Results at a Glance:

The kinetics of ruthenium (III) catalysed oxidation of reducing sugars viz. D(+) glucose, D(+) galactose, D(-) fructose, maltose and lactose by sodium metaperiodate have been studied in alkaline medium. The reaction followed almost a similar kinetics.

The results may be summarised as follows:

- The order of reaction with respect of sodium metaperiodate was found to be unity during a particular kinetic run. However, the observed rate constant ( $K_{obs}$ ) was found to decrease with an increase in  $[IO_4^-]$ .
- The results of effect of substrate and  $OH^-$  on the rate of oxidation was similar. the reaction was first order in substrate of  $OH^-$  at lower concentrations. However the order of reaction decreases from unity to zero at higher (Substrate) or  $[OH^-]$  .
- The rate is proportional to  $\{k' + k'' [RuCl_3]\}$  where  $k'$  and  $k''$  are rate constant for uncatalysed and catalysed path, respectively. The reactions were also proceeding in absence of the catalyst. However, in absence of the catalyst, the reactions were found to be extremely slow. The observed rate constant for uncatalysed path ( $k'$ ) i.e.  $k_{obs}$  at  $(RuCl_3) = 0$  was matching with the value of intercept of the plot of  $(k_{obs})$  versus  $(RuCl_3)$  in case of each reducing sugar.
- Effect of temperature has been studied at four different temperatures (35, 40, 45 and 50°C) and activation parameters

**Table- III I-1 : Absorbance of reaction mixture at 390 nm.**

$[IO_4^-] \times 10^4$	$[RuCl_3] = 3.0 \times 10^{-4}$ M $(OH^-) = 0.10$ M, at room temperature	$[Fructose] \times 10^4$	$[RuCl_3] = 3.0 \times 10^{-4}$ M $(OH^-) = 0.10$ M, after heating the solutions at $60^\circ C$ for 15 min then cooling at room temperature
M	Absorbance	M	Absorbance
Nil	0.94	Nil	1.20
1.0	0.80	1.0	1.15
2.0	0.66	2.0	1.05
3.0	0.50	4.0	0.91
4.0	0.38	6.0	0.93
5.0	0.14	8.0	0.96
6.0	0.45	10.0	0.98
8.0	0.51	12.0	1.00
10.0	0.58	16.0	1.10
12.0	0.60	18.0	1.10
16.0	0.61		
18.0	0.62		

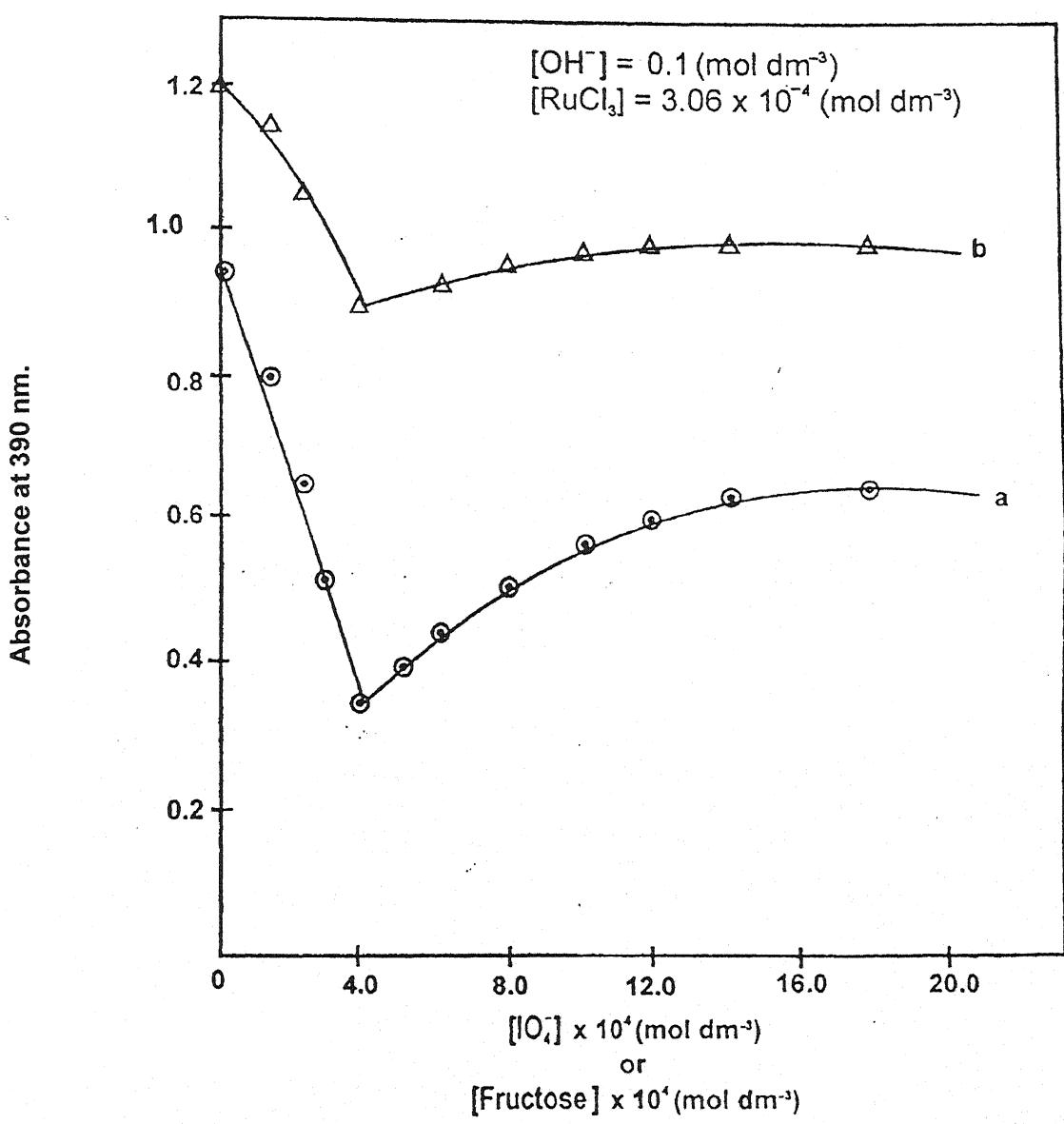


Fig. III I-1 : (a) Plot of Absorbance Vs  $[\text{IO}_4^-]$  at room temperature  
 (b) Plot of Absorbance Vs [Fructose] at  $60^\circ\text{C}$

have been evaluated (Table – III G–2). The same value of  $DG^\circ \backslash$  ( $94.34 \pm 1.0 \text{ kJ mol}^{-1}$ ) suggests the operation of a common mechanism for the oxidation process.

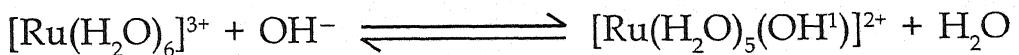
- The negligible effect of ionic strength was observed on the rate of reaction in case of each reducing sugars, suggesting involvement of at least one neutral species in rate determining step.
- At room temperature, the formation of  $\{\text{Ru}^{\text{III}} - \text{IO}_4^-\}$  complex has been confirmed by spectrophotometric evidence. It has also been observed that the complex between ruthenium (III) and reducing sugar under the similar conditions is also formed but at very high temperature.
- The reaction products were identified in both the conditions i.e. under the kinetic conditions and under stoichiometric condition. Under the kinetic conditions the formaldehyde and corresponding lower-acid was detected as the oxidation products of the reducing sugars. Under the stoichiometric condition, the formaldehyde is further oxidised in presence of excess of oxidant.

### III. K. Reacting species:

#### *Reactive species of catalysts:*

The electronic spectrum of ruthenium trichloride has shown<sup>75-</sup><sup>77</sup> that it exists in the hydrated form as  $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ . In alkaline medium the metal ions  $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$  are known<sup>78</sup> to exist as  $[\text{Ru}(\text{OH}^-)(\text{H}_2\text{O})_5]^{2+}$ .

A general formula  $[\text{Ru}(\text{OH})_x(\text{H}_2\text{O})_{6-x}]^{(3-x)+}$  where  $x < 6$  in place of  $[\text{Ru}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$  has also been considered in some case, yet there is no evidence for existence of the hexahydroxo species of ruthenium (III). Connick and Find<sup>77</sup> showed that the aqueous solution of  $\text{RuCl}_3$  contains the species  $\text{RuCl}_2^+$  which exists as the cis and trans-hydrated complexes,  $[\text{RuCl}_2(\text{H}_2\text{O})_4]^{2+}$ ,  $[\text{RuCl}_2(\text{H}_2\text{O})_4]^{2+}$  and  $[\text{RuCl}_4(\text{H}_2\text{O})_2]^{1-}$  have not been given importance. In alkaline medium generally  $[\text{Ru}(\text{H}_2\text{O})_5(\text{OH}^-)]^{2+}$  has been considered<sup>79</sup> as the reactive species of the catalyst according to the following equilibrium,

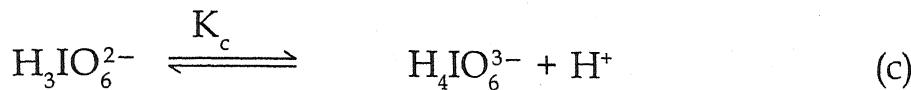
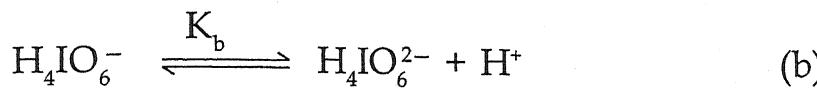
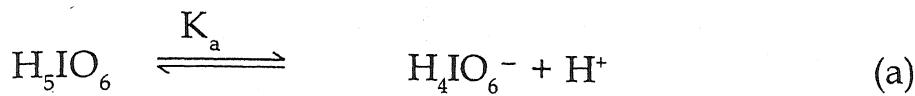


$[\text{Ru}(\text{H}_2\text{O})_5(\text{OH}^-)]^{2+}$  can undergo further substitution by hydroxide ion in higher alkali concentration. In the present investigations, therefore, the species  $[\text{Ru}(\text{H}_2\text{O})_5(\text{OH}^-)]^{2+}$  has been considered as the reactive species of the catalyst i.e. ruthenium (III).

#### *Reactive species of periodate:*

$\text{IO}_4^-$  is a powerful oxidising agent both in acidic and basic

media. Crouthamel *et al.*<sup>80</sup> suggested the following equilibria in aqueous solutions of periodate, which are pH controlled,



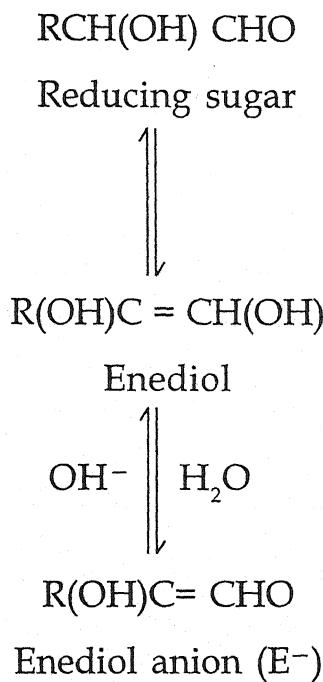
The dissociation constants  $K_a$ ,  $K_b$  and  $K_c$  at 25°C are reported<sup>81</sup> to be  $2.3 \times 10^{-2}$ ,  $4.35 \times 10^{-9}$  and  $1.5 \times 10^{-15}$ , respectively.

Among the above species the periodic acid  $\text{H}_5\text{IO}_6$  exist in acidic media and  $\text{H}_4\text{IO}_6^-$  near pH-7<sup>82</sup>. The UV and Raman spectral studies<sup>83-86</sup> indicate that in aqueous acid media (>5M), periodate mainly exists in the form of tetrahedral ( $\text{IO}_4^-$ ) and the octahedral ( $\text{H}_4\text{IO}_6^-$  and  $\text{H}_5\text{IO}_6$ ). At higher acidities protonated species  $\text{H}_6\text{IO}_6^+$  or  $\text{I}(\text{OH})_6^+$  exists. Galliford *et al.*<sup>85</sup> reported that at pH <2 the dilute periodate solutions are mainly in the form of  $\text{H}_5\text{IO}_6$  and  $\text{IO}_4^-$ . However, in the alkaline medium the solubility of sodium metaperiodate decreases with increase in [alkali]. The literature recorded and isolation of many species of periodate viz.  $\text{IO}_4^-$ ,  $[\text{O}_4\text{I}-\text{O}-\text{IO}_4]^{4-}$ ,  $[\text{H}_3\text{IO}_6]^{2-}$  and  $(\text{H}_4\text{IO}_6)^-$ . In alkaline medium the monoanion  $\text{H}_4\text{IO}_6^-$  species as reactive species of  $\text{IO}_4^-$  has been considered by several workers<sup>87-88</sup>. However, in the pH range employed in the present investigations, the reactive species of the oxidant are expected to be  $(\text{H}_3\text{IO}_6^{2-})$  and  $(\text{H}_2\text{IO}_6^{3-})$  with the following equilibrium,



### Reactive species of sugars :

In alkaline solution, sugars undergo enolization to form the enediolate<sup>89</sup> anion as,



(e)

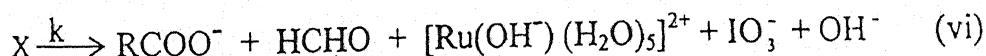
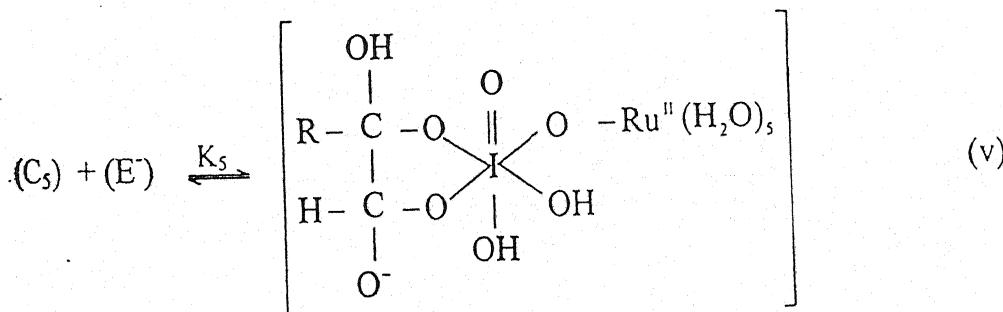
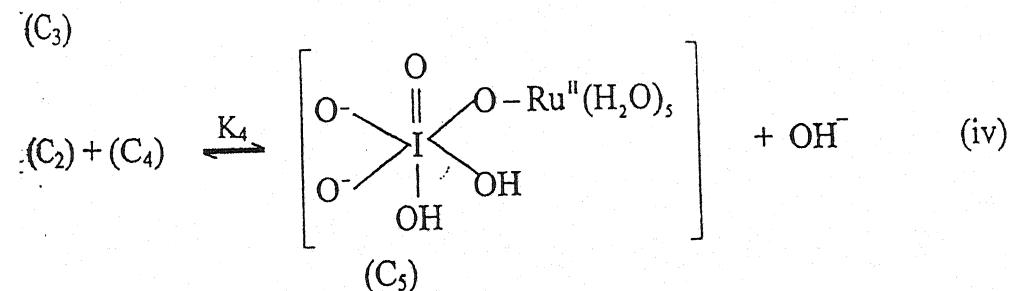
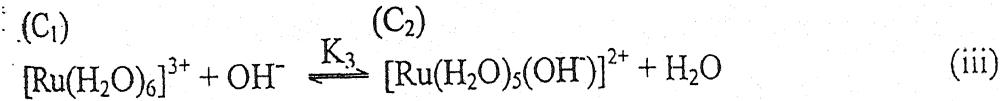
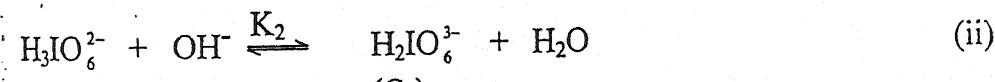
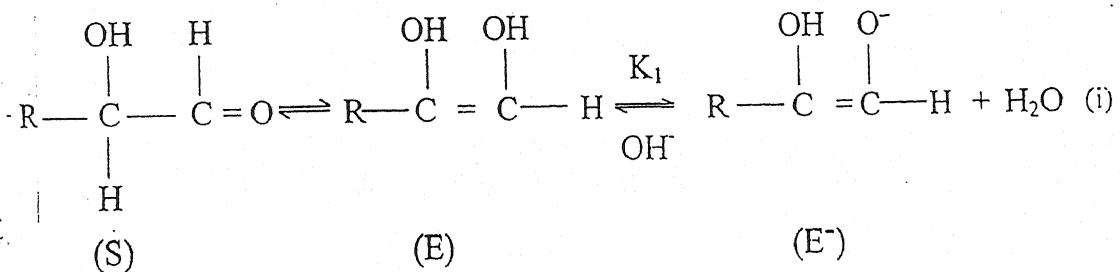
In absence of other reacants these enediol undergo epimerisation and insomersation (Lobry de – Bruyn Alberda Van Ekenstein transformation) to form a mixture of aldoses and ketoses<sup>89</sup>. Isbell and coworkers<sup>90</sup> Proposed that aldoses and ketoses generally yield mixture of Z – and E – enediols, the proportionality of which differ from sugar to sugar and experimental conditions viz. strength, nature of alkali and temperature etc. However, the enediol anion reacts with oxidant to form an intermediate<sup>30,36,38–40, 91</sup> which in turn

undergoes cleavage to form products. Therefore, in present investigations the enediol anion of the sugar has been considered as the reacting species of the reducing sugar.

### III L. Mechanism for Oxidation process:

On the basis of the reported literature, experimental results and evidence for the complex formation between ruthenium (III) and  $\text{IO}_4^-$ , a common mechanism for the oxidation of reducing sugars by  $\text{IO}_4^-$  in presence of ruthenium (III) may be summarised as given in Scheme—I

### Scheme – I



### III M. Derivation of Rate Law:

According to scheme I, the rate of disappearance of  $[\text{IO}_4^-]$  may be obtained as,

$$-\frac{D[\text{IO}_4^-]}{dt} = k [X] \quad (1)$$

considering the total concentration of  $\text{IO}_4^-$  may be obtained as,

$$[\text{IO}_4^-] = [C_1] + [C_2] \quad (2)$$

Where  $[C_2] = K_2 [\text{OH}^-] [C_1]$

( $K_2$  also includes water molecule

$[C_2]$  in terms of  $[\text{IO}_4^-]_t$  may be obtained as,

$$[C_2] = \frac{K_2 [\text{IO}_4^-]_t [\text{OH}^-]}{\{1 + K_2 [\text{OH}^-]\}} \quad (3)$$

Again the total concentration of the catalyst at any time is given by,

$$[\text{Cat}]_t = [C_3] + [C_4] + [C_5] + (X) \quad (4)$$

where ,

$$[C_4] = K_3 [C_3] [\text{OH}^-]$$

( $K_3$  also includes water molecule) (5)

$$\begin{aligned} [C_5] &= K_4 [C_2] C_4 / [\text{OH}^-] \\ &= \frac{K_2 K_3 K_4 [\text{OH}^-] [\text{IO}_4^-]_t [C_3]}{\{1 + K_2 [\text{OH}^-]\}} \end{aligned} \quad (6)$$

and

$$(X) = K_5 [C_5][E^-]$$

(where  $[E^-] = K_1 [S] [OH^-]$  from step (i))

or,

$$[X] = \frac{K_1 K_2 K_3 K_4 K_5 [OH^-]^2 [IO_4^-]_T [S] [C_3]}{\{1 + K_2 [OH^-]\}} \quad (7)$$

Thus] finding the value of  $[X]$  in terms of  $[Cat]_T$  the rate of disappearance of  $[IO_4^-]$  has been obtained as,

$$-\frac{d[IO_4^-]}{dt} = \frac{k K_1 K_2 K_3 K_4 K_5 [OH^-]^2 [S] [Cat]_T [IO_4^-]_T}{\{1 + K_2 [OH^-]\} \{1 + K_3 [OH^-] + K_2 K_3 [OH^-] [IO_4^-]_T \{1 + K_1 K_5 [S] [OH^-]\}\}} \quad (8)$$

taking  $(K_2 + K_3 [OH^-] + K_2 K_3 [OH^-]) \gg 1$

and  $K_1 K_5 [S] [OH^-] \gg 1$ , as suitable approximations in denominator of eq (8), the rate law (8) reduces to,

$$-\frac{d[IO_4^-]}{dt} = \frac{k K_1 K_2 K_3 K_4 K_5 [OH^-] [S] [Cat]_T [IO_4^-]_T}{(K_2 + K_3) + K_2 K_3 [OH^-] + K_1 K_2 K_3 K_4 K_5 [S] [OH^-] [IO_4^-]_T} \quad (9)$$

or

$$-\frac{d[IO_4^-]}{dt} = \frac{k K' [OH^-] [S] [Cat]_T [IO_4^-]_T}{(K_2 + K_3) + K_2 K_3 [OH^-] + K' [S] [OH^-] [IO_4^-]_T} \quad (10)$$

where,  $K' = K_1 K_2 K_3 K_4 K_5$ .

(103)

### **III N. Rate Law and experimental Results:**

The rate law (10) is in agreement with the experimental results, i.e. first order dependence of rate with respect to each, i.e. substrate,  $\text{OH}^-$  and oxidant at lower concentrations. The decrease in the observed rate constant ( $k_{\text{obs}}$ ) with an increase  $[\text{IO}_4^-]$  and a decrease in the order of reaction with respect to  $\text{OH}^-$  and substrate at higher  $[\text{OH}^-]$  and [substrate], respectively. The rate law is also indicates that the order of reaction with respect to catalyst is always unity. Thus the proposed mechanism and corresponding rate law explain all the experimental results.

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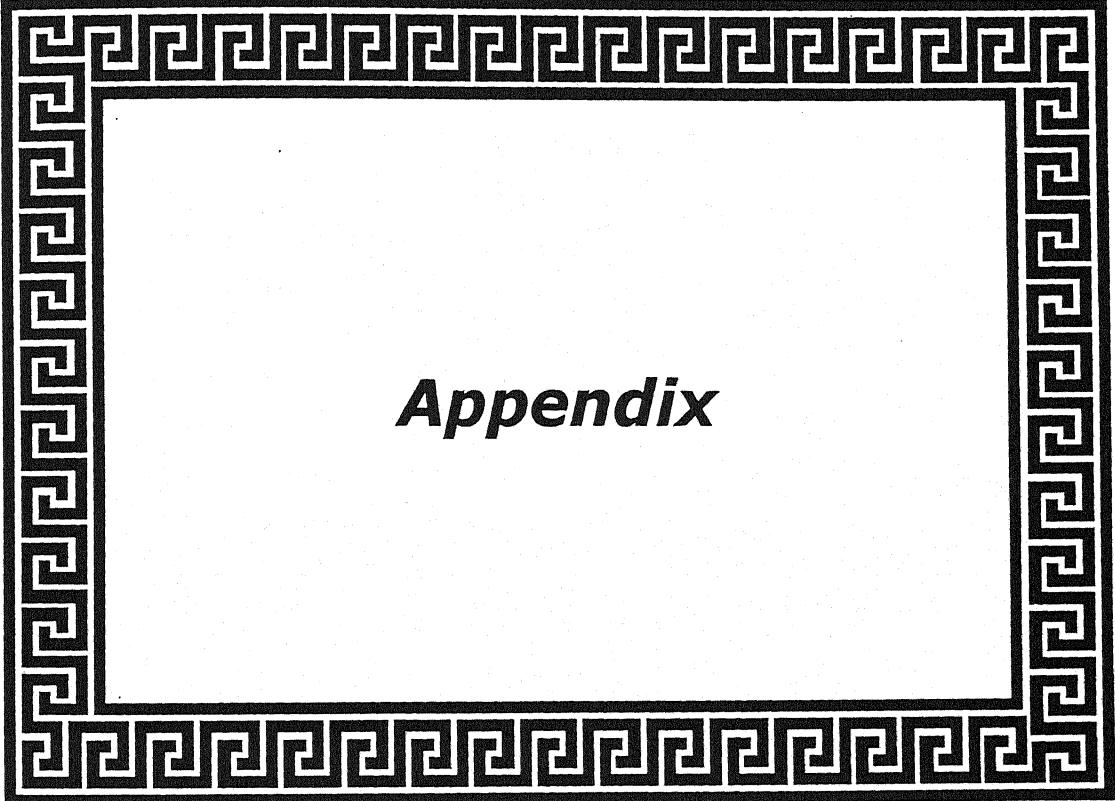
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## ***Appendix***

## Appendix III.1 : Effect of Variation of (Sodium metaperiodate) on the rate of oxidation of fructose at 40°C

$[S] = 2.0 \times 10^{-2}$ , $[\text{OH}^-] = 0.1$ , $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ and $[\text{Hypo}] = 1.0 \times 10^{-2}$		Time $\downarrow$ $\rightarrow [\text{IO}_4^-] \times 10^3 =$						
Time $\downarrow$ (min)	$\rightarrow [\text{IO}_4^-] \times 10^3 =$	V	Time $\downarrow$ (min)	V	Time $\downarrow$ (min)	V	Time $\downarrow$ (min)	V
(a)			(b)		(c)		(d)	
0	3.4	0	5.1	7.0	0	10.2	12.8	
2	3.1	5	4.1	5.7	10	7.9	10.8	
4	2.8	10	3.3	4.8	20	6.1	9.3	
6	2.5	15	2.7	4.1	30	4.7	7.7	
8	2.3	20	2.2	3.5	40	3.8	6.5	
10	2.1	25	1.7	2.9	50	2.9	5.6	
12	1.9	30	1.4	2.4	60	2.3	4.7	
14	1.7	35	1.2	2.1	40	1.7	4.0	
16	1.6	40	-	1.7	80	-	3.4	

(116)

The concentrations of the reactants are in mol  $\text{dm}^{-3}$ ; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.

## Appendix III.2 : Effect of Variation of (Sodium metaperiodate) on the rate of oxidation of Glucose at 40°C

[S] = $2.0 \times 10^{-2}$ , $[\text{OH}^-] = 0.1$ , $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ and $[\text{Hypo}] = 1.0 \times 10^{-2}$		Time ↓ → $[\text{IO}_4^-] \times 10^3$ = (min)	V	V	Time ↓ (min)	3.0 V	4.0 V
(a)	(b)						
0	3.4	5.1	7.0	0	1.2	12.8	
5	2.8	4.3	6.1	10	8.5	11.2	
10	2.3	3.7	5.4	20	6.8	9.6	
15	1.9	3.1	4.6	30	5.6	8.5	
20	1.5	2.6	4.1	40	4.5	7.3	
25	1.3	2.2	3.5	50	3.6	6.4	
30	-	1.9	3.0	60	3.0	5.6	
35	-	1.6	2.6	70	2.4	4.8	
40	-	1.3	2.2	80	1.9	4.2	

(117)

The concentrations of the reactants are in mol  $\text{dm}^{-3}$ ; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.

### Appendix III.3 : Effect of Variation of (Sodium metaperiodate) on the rate of oxidation of Galactose at 40°C

$[S] = 2.0 \times 10^{-2}$ , $[\text{OH}^-] = 0.1$ , $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ and $[\text{Hypo}] = 1.0 \times 10^{-2}$		Time $\downarrow$ $\rightarrow [\text{IO}_4^-] \times 10^3 =$					Time $\downarrow$				
Time $\downarrow$ (min)	V	1.0 V	Time $\downarrow$ (min)	1.5 V	2.0 V	Time $\downarrow$ (min)	3.0 V	4.0 V			
(a)		(b)		(c)		(d)		(e)			
0	3.4	0	5.1	7.0	0	0	10.2	12.8			
2	3.0	5	4.1	5.7	10	10	8.3	11.4			
4	2.9	10	3.4	5.1	20	20	6.7	9.9			
6	2.6	15	2.8	4.2	30	30	5.4	8.5			
8	2.4	20	2.1	3.7	40	40	4.3	7.4			
10	2.1	25	1.8	3.0	50	50	3.5	6.4			
12	1.9	30	1.4	2.7	60	60	2.8	5.5			
14	1.8	35	1.2	2.3	70	70	2.2	4.8			
16	1.7	40	-	1.9	80	80	1.9	4.2			
18	1.4	-	-	-	-	-	-	-			

(118)

The concentrations of the reactants are in  $\text{mol dm}^{-3}$ ; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.

## Appendix III.4 : Effect of Variation of (Sodium metaperiodate on the rate of oxidation of Maltose at 40°C

[S] = $2.0 \times 10^{-2}$ , $[\text{OH}^-] = 0.1$ , $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ and $[\text{Hypo}] = 1.0 \times 10^{-2}$		Time $\downarrow$ $\rightarrow [\text{IO}_4^-] \times 10^3 =$				
Time $\downarrow$ (min)	$\rightarrow [\text{IO}_4^-] \times 10^3 =$	1.0 V	1.5 V	2.0 V	Time $\downarrow$ (min)	3.0 V
	(a)	(b)	(c)		(d)	(e)
0	3.4	5.1	7.0	0	1.2	12.8
5	2.7	4.3	6.0	10	8.1	11.1
10	2.1	3.6	5.2	20	6.4	9.5
15	1.7	3.0	4.4	30	5.1	8.3
20	1.3	2.6	3.9	40	4.0	7.8
25	-	2.1	3.3	50	3.2	5.9
30	-	1.8	2.7	60	2.6	5.2
35	-	1.5	2.4	70	2.0	4.4
40	-	1.3	2.0	80	1.6	3.8
45	-	-	-	-	-	-
50	-	-	-	1.5	-	-

(119)

The concentrations of the reactants are in  $\text{mol dm}^{-3}$ ; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.

## Appendix III.5 : Effect of Variation of (Sodium metaperiodate) on the rate of oxidation of Lactose at 40°C

Time ↓ (min)	$\rightarrow [\text{IO}_4^-] \times 10^3 =$				Time ↓ (min)	3.0 V	4.0 V
	1.0 V	1.5 V	2.0 V	(a)			
0	3.4	5.1	7.0	0		10.2	12.8
5	2.9	4.5	6.3	10		8.3	11.1
10	2.5	3.9	5.6	20		6.7	9.7
15	2.2	3.4	5.0	30		5.4	8.5
20	1.9	3.0	4.4	40		4.5	7.3
25	1.6	2.7	3.8	50		3.7	6.5
30	1.4	2.3	3.4	60		3.0	5.7
35	1.2	2.0	3.0	70		2.4	4.9
40	-	1.8	2.7	80		2.0	4.3
45	-	1.5	-	-		-	-
50	-	-	2.1	-		-	-

(120)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.

## Appendix III.6 : Effect of Variation of (Fructose) on the rate of oxidation of Fructose at 40°C

[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [OH <sup>-</sup> ]=0.1, [RuCl <sub>3</sub> ]=3.0x10 <sup>-4</sup> and [Hypo] = 1.0x10 <sup>-2</sup>		Time →[S]x10 <sup>2</sup> =								
(min)	(a)	V	V	1.0	Time	1.5	2.0	3.0	4.0	5.0
		V	↓	V	V	V	V	V	V	
0	7.0	7.0	7.0	0	7.0	7.0	7.0	7.0	7.0	7.0
10	6.5	6.2	5.7	5	6.1	5.7	5.6	5.5	5.4	5.4
20	6.0	5.4	4.8	10	5.4	4.8	4.6	4.4	4.2	4.2
30	5.5	4.8	3.8	15	4.6	4.1	3.8	3.5	3.3	3.3
40	5.2	4.2	3.1	20	4.1	3.5	3.0	2.8	2.6	2.6
50	4.8	3.7	2.6	25	3.6	2.9	2.4	2.2	2.0	2.0
60	4.5	3.3	2.1	30	3.1	2.4	2.0	1.7	1.6	1.6
70	4.1	2.9	1.7	35	2.7	2.1	1.6	1.4	1.2	1.2
80	3.8	2.5	-	40	2.3	1.7	1.3	-	-	-
	-	-	-	45	2.0	-	-	-	-	-

(121)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.

## Appendix III.7 : Effect of Variation of (Glucose) on the rate of oxidation of Glucose at 40°C

		[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [OH <sup>-</sup> ]=0.1, [RuCl <sub>3</sub> ]=3.0x10 <sup>-4</sup> and [Hypo] = 1.0x10 <sup>-2</sup>						
Time ↓ (min)	→[S]x10 <sup>2</sup> = V	1.0 V	1.5 V	Time ↓ (min)	2.0 V	3.0 V	4.0 V	5.0 V
(a)	(b)	(c)	(d)	(e)	(f)	(g)		
0	7.0	7.0	7.0	0	7.0	7.0	7.0	7.0
10	6.5	6.1	5.8	5	6.1	5.9	5.6	5.3
20	5.8	5.3	4.6	10	5.4	4.9	4.5	4.3
30	5.4	4.5	3.8	15	4.6	4.1	3.7	3.4
40	4.9	3.9	3.1	20	4.1	3.4	2.9	2.7
50	4.5	3.5	2.6	25	3.5	2.9	2.4	2.1
60	4.3	3.0	2.1	30	3.0	2.4	1.9	1.7
70	3.9	2.6	1.7	35	2.6	2.0	1.6	1.4
80	3.7	2.3	1.4	40	2.2	1.7	1.3	-
				45	-	1.4	-	-
				50	1.7	-	-	-

(122)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.

**Appendix III.8 : Effect of Variation of (Galactose) on the rate of oxidation of Galactose at 40°C**

Time		$\rightarrow [S] \times 10^2 =$		0.5	1.0	1.5	Time	2.0	3.0	4.0	5.0
		V	V	V	V	V	V	V	V	V	V
(min)		(a)	(b)	(c)	(min)		(d)	(e)	(f)	(g)	
0		7.0	7.0	7.0	0		7.0	7.0	7.0	7.0	
10		6.3	5.7	5.3	5		5.7	5.6	5.5	5.4	
20		5.4	4.5	4.1	10		5.1	4.7	4.5	4.3	
30		4.6	3.7	3.2	15		4.2	3.9	3.6	3.4	
40		4.1	2.9	2.5	20		3.7	3.3	2.9	2.7	
50		3.7	2.3	1.9	25		3.0	2.7	2.3	2.1	
60		3.1	1.9	1.5	30		2.7	2.2	1.9	1.6	
70		2.8	1.5	-	35		2.3	1.8	1.5	1.3	
80		2.4	-	-	40		1.9	1.5	-	-	

(123)

The concentrations of the reactants are in  $\text{mol dm}^{-3}$ ; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.

## Appendix III.9 : Effect of Variation of (Maltose) on the rate of oxidation of Maltose at 40°C

		[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [OH <sup>-</sup> ]=0.1, [RuCl <sub>3</sub> ]=3.0x10 <sup>-4</sup> and [Hypo] = 1.0x10 <sup>-2</sup>							
Time ↓ (min)	→[S]x10 <sup>2</sup> = V	0.5 V	1.0 V	Time ↓ (min)	1.5 V	2.0 V	3.0 V	4.0 V	5.0 V
(a)	(b)	(c)	(d)	(e)	(f)	(g)			
0	7.0	7.0	0	7.0	7.0	7.0	7.0	7.0	7.0
10	6.4	6.0	5	6.3	6.0	5.8	5.6	5.6	5.2
20	5.8	4.8	10	5.5	5.2	4.8	4.5	4.5	4.2
30	5.2	4.0	15	4.8	4.4	4.0	3.8	3.8	3.4
40	4.6	3.4	20	4.3	3.9	3.3	3.0	3.0	2.7
50	4.2	2.8	25	3.8	3.3	2.8	2.4	2.4	2.1
60	3.8	2.3	30	3.3	2.7	2.3	2.0	2.0	1.6
70	3.4	2.0	35	2.9	2.4	1.9	1.6	1.6	1.3
80	3.0	1.6	40	2.6	2.0	1.6	1.3	1.3	-
		45	-	-	1.3	-	-	-	-
		50	2.0	1.5	-	-	-	-	-

(124)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.

## Appendix III.10 : Effect of Variation of (Lactose) on the rate of oxidation of Lactose at 40°C

		[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [OH <sup>-</sup> ]=0.1, [RuCl <sub>3</sub> ]=3.0x10 <sup>-4</sup> and [Hypo] = 1.0x10 <sup>-2</sup>							
Time ↓ (min)	→[S]x10 <sup>2</sup> = V	0.5 V	1.0 V	1.5 V	Time ↓ (min)	2.0 V	3.0 V	4.0 V	5.0 V
(a)	(b)	(c)	(d)	(e)	(f)	(g)			
0	7.0	7.0	7.0	0	7.0	7.0	7.0	7.0	7.0
10	6.8	6.4	5.8	5	6.3	6.1	5.9	5.8	
20	6.5	5.7	4.8	10	5.6	5.3	5.1	4.8	
30	6.1	5.1	4.0	15	5.0	4.5	4.3	4.2	
40	5.8	4.6	3.4	20	4.4	3.8	3.7	3.5	
50	5.6	4.1	2.8	25	3.8	3.4	3.1	2.9	
60	5.3	3.7	2.3	30	3.4	2.9	2.7	2.7	
70	5.0	3.3	1.9	35	3.0	2.5	2.2	2.1	
80	4.7	2.9	1.6	40	2.7	2.2	1.9	1.7	
				45	-	1.9	1.6	1.5	
				50	2.1	-	-	-	

(125)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

## Appendix III.11 : Effect of Variation of (OH<sup>-</sup>) on the rate of oxidation of Fructose at 40°C

[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [S]=0.2x10 <sup>-2</sup> , [RuCl <sub>3</sub> ]=3.0x10 <sup>-4</sup> and [Hypo] = 1.0x10 <sup>-2</sup>													
Time ↓	→[OH <sup>-</sup> ]x10 = V	Time ↓	Time V	1.0 V	1.5 V	Time ↓	2.0 V	3.0 V	4.0 V	5.0 V			
(min)	(a)	(min)	(b)	(c)	(min)	(d)	(e)	(f)	(g)				
0	7.0	0	7.0	7.0	0	7.0	7.0	7.0	7.0	7.0			
10	5.8	5	5.9	5.6	5.2	2	6.0	5.8	5.7				
20	4.8	10	5.0	4.3	3.8	4	5.1	4.7	4.5				
30	4.0	15	4.1	3.4	2.8	6	4.3	3.8	3.6				
40	3.4	20	3.4	2.7	2.1	8	3.6	3.0	2.9				
50	2.9	25	2.9	2.1	1.6	10	3.0	2.5	2.2				
60	2.3	30	2.4	1.6	1.5	12	2.6	2.0	1.9				
70	1.9	35	2.0	1.3	-	14	2.2	1.7	1.5				
80	1.6	40	4\1.7	-	-	16	1.8	1.4	1.1				
	-	45	1.4	-	-	18	1.6	-	-				

(126)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

**Appendix III.12 : Effect of Variation of (OH<sup>-</sup>) on the rate of oxidation of Glucose at 40°C**

[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [S]=0.2x10 <sup>-2</sup> , [RuCl <sub>3</sub> ]=3.0x10 <sup>-4</sup> and [Hypo] = 1.0x10 <sup>-2</sup>								
Time → [OH <sup>-</sup> ]x10 =	Time	1.0	1.5	2.0	3.0	4.0	5.0	
↓	V	↓	V	V	V	V	V	
(min)	(a)	(min)	(b)	(c)	(d)	(e)	(f)	(g)
0	7.0	0	7.0	7.0	7.0	7.0	7.0	7.0
10	6.1	5	6.2	6.0	5.8	5.6	5.4	5.3
20	5.3	10	5.4	5.1	4.8	4.6	4.4	4.2
30	4.6	15	4.8	4.3	4.0	3.7	3.5	3.3
40	4.0	20	4.3	3.7	3.3	3.0	2.7	2.5
50	3.5	25	3.8	3.1	2.7	2.4	2.1	2.0
60	3.0	30	3.3	2.6	2.2	1.9	1.7	1.5
70	2.6	35	2.8	2.2	1.9	1.5	1.3	1.2
80	2.3	40	2.5	1.9	1.5	1.3	-	-
	45		2.3	1.6	1.3	-	-	-

(127)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

### Appendix III.13 : Effect of Variation of $(\text{OH}^-)$ on the rate of oxidation of Galactose at $40^\circ\text{C}$

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ ,  $[\text{S}] = 0.2 \times 10^{-2}$ ,  $[\text{RuCl}_3] = 3.0 \times 10^{-4}$  and  $[\text{Hypo}] = 1.0 \times 10^{-2}$

Time (min)	$\rightarrow [\text{OH}^-] \times 10 =$ V	Time $\downarrow$	1.0 V	1.5 V	2.0 V	3.0 V	4.0 V	5.0 V
(a)	(b)	(c)	(d)	(e)	(f)	(g)		
0	7.0	0	7.0	7.0	7.0	7.0	7.0	7.0
10	5.7	5	5.8	5.7	5.5	5.4	5.2	4.9
20	4.7	10	5.0	4.7	4.4	4.2	3.8	3.7
30	3.9	15	4.1	3.8	3.5	3.2	2.9	2.6
40	3.1	20	3.7	3.2	2.8	2.4	2.0	1.9
50	2.6	25	3.0	2.6	2.2	1.9	1.6	1.3
60	2.0	30	2.7	2.2	1.8	1.5	1.2	-
70	1.7	35	2.3	1.8	1.4	-	-	-
	40	40	1.9	1.5	-	-	-	-

(128)

The concentrations of the reactants are in mol  $\text{dm}^{-3}$ ; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

## Appendix III.14 : Effect of Variation of $(\text{OH}^-)$ on the rate of oxidation of Maltose at $40^\circ\text{C}$

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ , $[\text{S}] = 0.2 \times 10^{-2}$ , $[\text{RuCl}_3] = 3.0 \times 10^{-4}$ and $[\text{Hypo}] = 1.0 \times 10^{-2}$						
Time	$\rightarrow [\text{OH}^-] \times 10 =$	1.0	2.0	Time	3.0	4.0
$\downarrow$	V	V	V	V	V	V
(min)	(a)	(b)	(min)	(c)	(d)	(e)
0	7.0	7.0	0	7.0	7.0	7.0
10	6.1	5.4	5	5.6	5.5	5.4
20	5.3	4.3	10	4.9	4.7	4.4
30	4.5	3.3	15	4.0	3.8	3.4
40	4.0	2.6	20	3.3	3.0	2.6
50	3.5	2.0	25	2.8	2.4	2.0
60	3.0	1.6	30	2.3	1.9	1.6
70	2.6	1.3	35	1.9	1.6	1.3
80	2.2	-	40	1.6	1.3	-
			45	1.3	-	-

(129)

The concentrations of the reactants are in  $\text{mol dm}^{-3}$ ; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

## Appendix III.15 : Effect of Variation of (OH<sup>-</sup>) on the rate of oxidation of Laltose at 40°C

[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [S]=0.2x10 <sup>-2</sup> , [RuCl <sub>3</sub> ]=3.0x10 <sup>-4</sup> and [Hypo] = 1.0x10 <sup>-2</sup>		Time →[OH <sup>-</sup> ]x10 = 1.0      2.0      3.0      4.0      Time      6.0      8.0      10.0						
↓		V	V	V	V	V	V	V
(min)	(a)	(b)	(c)	(d)	(min)	(e)	(f)	(g)
0	7.0	7.0	7.0	0	0	7.0	7.0	7.0
10	6.4	5.9	5.6	5.3	5	5.9	5.7	5.4
20	5.7	5.2	4.6	4.1	10	5.0	4.7	4.4
30	5.1	4.4	3.8	3.1	15	4.2	3.9	3.6
40	4.5	3.8	3.0	2.4	20	3.7	3.3	2.9
50	4.0	3.3	2.5	1.9	25	3.0	2.8	2.3
60	3.7	2.8	2.0	1.5	30	2.6	2.3	1.9
70	3.3	2.3	1.7	-	35	2.2	1.9	1.5
80	2.9	2.0	-	-	40	1.9	1.6	1.3
					45	1.6	1.3	-

(130)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

## Appendix III.16 : Effect of Variation of (RuCl<sub>3</sub>) on the rate of oxidation of Fructose at 40°C

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ , $[\text{S}] = 0.2 \times 10^{-2}$ , $[\text{OH}^-] = 0.1$ and $[\text{Hypo}] = 1.0 \times 10^{-2}$					
Time ↓ (min)	$\rightarrow [\text{RuCl}_3] \times 10^4 =$ V	1.5 V	Time ↓ (min)	3.0 V	4.5 V
(a)	(b)	(c)	(d)	(e)	(f)
0	7.0	7.0	0	7.0	7.0
10	6.3	5.7	5	5.7	5.5
20	5.7	4.6	10	4.8	4.3
30	5.2	3.8	15	4.1	3.4
40	4.7	3.1	20	3.5	2.7
50	4.2	2.6	25	2.9	2.1
60	3.8	2.1	30	2.4	1.6
70	3.5	1.7	35	2.1	1.3
80	3.2	-	40	1.7	-

(131)

The concentrations of the reactants are in mol dm<sup>-3</sup>, V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

**Appendix III.17 : Effect of variation of  $(\text{RuCl}_3)$  on the rate of oxidation of Glucose at  $40^\circ\text{C}$**

$[\text{IO}_4^-] = 2.0 \times 10^{-3}$ , $[\text{S}] = 0.2 \times 10^{-2}$ , $[\text{OH}^-] = 0.1$ and $[\text{Hypo}] = 1.0 \times 10^{-2}$		$\rightarrow [\text{RuCl}_3] \times 10^4 =$					
Time (min)	Nil V	1.5 V	Time $\downarrow$	3.0 V	4.5 V	6.0 V	9.0 V
(a)	(b)	(min)	(c)	(d)	(e)	(f)	
0	7.0	7.0	0	7.0	7.0	7.0	7.0
10	6.4	5.9	5	6.1	5.8	5.5	5.2
20	5.9	5.2	10	5.4	4.7	4.4	4.0
30	5.4	4.4	15	4.6	4.0	3.5	3.0
40	5.1	3.8	20	4.1	3.3	2.8	2.2
50	4.5	3.2	25	3.5	2.8	2.2	1.7
60	4.3	2.8	30	3.0	2.3	1.8	1.3
70	3.9	2.3	35	2.6	1.9	1.4	-
80	3.6	2.0	40	2.2	1.6	-	-
			45	-	1.3	-	-
			50	1.7	-	-	-

(132)

The concentrations of the reactants are in mol  $\text{dm}^{-3}$ ; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

**Appendix III.18 : Effect of Variation of (RuCl<sub>3</sub>) on the rate of  
oxidation of Galactose at 40°C**

[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [S]=0.2x10 <sup>-2</sup> , [OH <sup>-</sup> ]=0.1 and [Hypo] = 1.0x10 <sup>-2</sup>		Time → [RuCl <sub>3</sub> ]x10 <sup>4</sup> = Nil					
Time ↓ (min)	V	V	Time ↓ (min)	3.0	4.5	6.0	9.0
(a)	(b)	(c)	(d)	(e)	(f)		
0	7.0	0	7.0	7.0	7.0	7.0	7.0
10	6.2	5.7	5	5.7	5.5	5.4	5.2
20	5.5	4.7	10	5.1	4.7	4.3	4.0
30	4.8	3.9	15	4.2	3.8	3.4	3.0
40	4.3	3.1	20	3.7	3.2	2.7	2.3
50	3.8	2.6	25	3.0	2.6	2.1	1.7
60	3.4	2.1	30	2.7	2.2	1.7	1.3
70	3.0	1.7	35	2.3	1.8	1.3	-
80	2.7	-	40	1.9	1.5	-	-

(133)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

## Appendix III.19 : Effect of Variation of (RuCl<sub>3</sub>) on the rate of oxidation of Maltose at 40°C

[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [S]=0.2x10 <sup>-2</sup> , [OH <sup>-</sup> ]=0.1 and [Hypo] = 1.0x10 <sup>-2</sup>								
Time ↓ (min)	→[RuCl <sub>3</sub> ]x10 <sup>4</sup>	Nil V	1.5 V	Time ↓ V	3.0 V	4.5 V	6.0 V	9.0 V
	(a)	(b)	(min)	(c)	(d)	(e)	(f)	
0		7.0	7.0	0	7.0	7.0	7.0	7.0
10	6.4	5.7	5	6.0	5.7	5.3	4.8	
20	5.7	4.6	10	5.2	4.6	4.1	3.4	
30	5.1	3.9	15	4.4	3.8	2.5	2.3	
40	4.4	3.1	20	3.9	3.0	2.3	1.6	
50	4.2	2.6	20	3.3	2.4	1.8	1.1	
60	3.8	2.1	25	2.7	2.0	1.4	-	
70	3.4	1.7	30	2.4	1.6	-	-	
80	3.0	-	35	2.0	1.3	-	-	
			40	-	-	-	-	
			45	1.5	-	-	-	
			50					

(134)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

## Appendix III.20 : Effect of Variation of (RuCl<sub>3</sub>) on the rate of oxidation of Lactose at 40°C

[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [S]=0.2x10 <sup>-2</sup> , [OH <sup>-</sup> ]=0.1 and [Hypo] = 1.0x10 <sup>-2</sup>		Time →[RuCl <sub>3</sub> ]x10 <sup>4</sup> = Nil						Time →[RuCl <sub>3</sub> ]x10 <sup>4</sup> = V					
(min)	(a)	(b)	(c)	(d)	(e)	(f)	V	V	V	V	V	V	V
							1.5	↓	3.0	4.5	6.0	9.0	
0		7.0	7.0	0	7.0	7.0			7.0	7.0	7.0	7.0	
10	6.1	5.8	5	6.3	6.0	5.8			6.0	5.8	5.6	5.6	
20	5.3	4.8	10	5.6	5.2	4.8			5.6	5.2	4.8	4.5	
30	4.6	4.0	15	5.0	4.5	4.0			5.0	4.5	4.0	3.7	
40	4.0	3.4	20	4.4	3.9	3.4			4.4	3.9	3.4	3.0	
50	3.5	2.8	25	3.8	3.4	2.9			3.8	3.4	2.9	2.4	
60	3.1	2.3	30	3.4	2.9	2.4			3.4	2.9	2.4	2.0	
70	2.7	1.9	35	3.0	2.5	2.0			3.0	2.5	2.0	1.6	
80	2.3	1.6	40	2.7	2.2	1.7			2.7	2.2	1.7	1.3	
			45	-	-	1.4						-	
			50	2.1	1.6	-						-	

(135)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

## Appendix III.21 : Effect of Variation of Temperature on the rate of oxidation of Fructose

$[IO_4^-] = 2.0 \times 10^{-3}$ , $[S] = 0.2 \times 10^{-2}$ , $[OH^-] = 0.1$ , $[RuCl_3] = 3.0 \times 10^{-4}$ , and $[Hypo] = 1.0 \times 10^{-2}$						
Time ↓ (min)	→Temp. = V (a)	35°C ↓ (min)	Time 40°C V (b)	45°C V (c)	50°C V (d)	
0		7.0	0	7.0	7.0	7.0
10		5.7	5	5.7	5.4	4.8
20		4.6	10	4.8	4.2	3.3
30		3.8	15	4.1	3.4	2.3
40		3.0	20	3.5	2.7	1.6
50		2.4	25	2.9	1.6	1.1
60		2.0	30	2.4	1.5	-
70		1.6	35	2.1	-	-
			40	1.7	-	-

(136)

The concentrations of the reactants are in  $mol\ dm^{-3}$ ; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

## Appendix III.22 : Effect of Variation of Temperature on the rate of oxidation of Glucose

		[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [S]=0.2x10 <sup>-2</sup> , [OH <sup>-</sup> ]=0.1, [RuCl <sub>3</sub> ]= 3.0x10 <sup>-4</sup> , and [Hypo] = 1.0x10 <sup>-2</sup>					
Time ↓ (min)	→Temp. =	35°C V (a)	Time ↓ (min)	40°C V (b)	45°C V (c)	50°C V (d)	7.0
0		7.0	0	7.0	7.0	7.0	7.0
10		6.4	5	6.1	5.5	4.8	
20		5.8	10	5.4	4.4	3.6	
30		5.3	15	4.6	3.6	2.5	
40		4.8	20	4.1	2.8	1.8	
50		4.5	25	3.5	2.2	1.3	
60		4.1	30	3.0	1.7	-	
70		3.8	35	2.6	1.4	-	
80		3.5	40	2.2	-	-	
			45	-	-	-	
			50	1.7	-	-	

(137)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

## Appendix III.23 : Effect of Variation of Temperature on the rate of oxidation of Galactose

		[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [S]=0.2x10 <sup>-2</sup> , [OH <sup>-</sup> ]=0.1, [RuCl <sub>3</sub> ]= 3.0x10 <sup>-4</sup> , and [Hypo] = 1.0x10 <sup>-2</sup>					
Time ↓ (min)	→Temp. = V (a)	35°C Time ↓ (min)	40°C Time ↓ (b)	45°C Time ↓ (c)	50°C Time ↓ (d)		
0	7.0	0	7.0	7.0	7.0	7.0	7.0
10	6.1	5	5.7	5.5	4.8		
20	5.2	10	5.1	4.4	3.3		
30	4.4	15	4.2	3.4	2.3		
40	3.8	20	3.7	2.7	1.6		
50	3.2	25	3.0	2.0	-		
60	2.8	30	2.7	1.6	-		
70	2.3	35	2.3	1.3	-		
80	2.0	40	1.9	-	-		

(138)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

## Appendix III.24 : Effect of Variation of Temperature on the rate of oxidation of Maltose

		[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [S]=0.2x10 <sup>-2</sup> , [OH <sup>-</sup> ]=0.1, [RuCl <sub>3</sub> ]= 3.0x10 <sup>-4</sup> , and [Hypo] = 1.0x10 <sup>-2</sup>					
Time ↓ (min)	→Temp. = V (a)	35°C		40°C		45°C	
		Time ↓ (min)	V (b)	V (c)	V (d)	V	
0	7.0	0	7.0	7.0	7.0	7.0	7.0
10	6.1	5	6.0	5.4	5.4	4.4	
20	5.3	10	5.2	4.2	4.2	3.0	
30	4.7	15	4.4	3.3	3.3	1.9	
40	4.1	20	3.9	2.6	2.6	1.3	
50	3.7	25	3.3	2.0	2.0	-	
60	3.2	30	2.7	1.6	1.6	-	
70	2.8	35	2.4	1.3	1.3	-	
80	2.5	40	2.0	-	-	-	
		45	-	-	-	-	
		50	1.5	-	-	-	

(139)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

## Appendix III.25 : Effect of Variation of Temperature on the rate of oxidation of Lactose

		[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [S]=0.2x10 <sup>-2</sup> , [OH <sup>-</sup> ]=0.1, [RuCl <sub>3</sub> ]= 3.0x10 <sup>-4</sup> , and [Hypo] = 1.0x10 <sup>-2</sup>					
Time ↓ (min)	→Temp. = V (a)	35°C ↓ (min)	Time 40°C V (b)	45°C V (c)	50°C V (d)		
0	7.0	0	7.0	7.0	7.0	7.0	7.0
10	6.4	5	6.3	5.8	5.8	58.2	
20	5.8	10	5.6	4.8	4.8		
30	5.3	15	5.0	4.0	4.0	3.9	
40	4.8	20	4.4	3.4	3.4	2.9	
50	4.5	25	3.8	2.8	2.8	2.2	
60	4.1	30	3.4	2.4	2.4	1.6	
70	3.8	35	3.0	1.9	1.9		
80	3.4	40	2.7	1.6	1.6		
		45	-	1.4	1.4		
		50	2.1	-	-		

(140)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

## Appendix III.26 : Effect of Variation of [Sodium perchlorate] on the rate of oxidation of Fructose at 40°C

Time ↓ (min)	[NaClO <sub>4</sub> ] × 10 = V (a)	Nil V (b)	0.5 V (c)	1.0 V (d)	1.5 V (e)	2.0 V
0	7.0	7.0	7.0	7.0	7.0	7.0
5	5.7	5.7	5.6	5.6	5.6	5.5
10	4.8	4.8	4.7	4.7	4.8	4.7
15	4.1	4.0	4.1	4.0	4.0	3.9
20	3.5	3.4	3.5	3.5	3.5	3.4
25	2.9	2.9	2.9	2.8	2.8	2.8
30	2.4	2.5	2.5	2.5	2.3	2.3
35	2.1	2.0	1.9	1.9	1.8	1.8
40	1.7	1.7	1.6	1.5	1.4	1.4

(141)

The concentrations of the reactants are in mol dm<sup>-3</sup>, V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

## Appendix III.27 : Effect of Variation of [Sodium perchlorate] on the rate of oxidation of Glucose at 40°C

Time ↓ (min)	[NaClO <sub>4</sub> ] × 10 = V (a)	Nil V (b)	0.5 V (c)	1.0 V (d)	1.5 V (e)	2.0 V
0	7.0	7.0	7.0	7.0	7.0	7.0
5	6.1	6.1	6.2	6.0	-	5.8
10	5.4	5.3	5.2	5.2	-	5.1
15	4.6	4.5	4.6	4.4	-	4.3
20	4.1	4.1	4.0	4.0	-	3.9
25	3.5	3.4	3.3	3.4	-	3.3
30	3.0	2.9	3.0	2.9	-	2.8
35	2.6	2.6	2.6	2.5	-	2.4
40	2.2	2.1	2.2	2.0	-	2.0
45	-	-	-	-	-	1.8
50	1.7	1.6	1.7	1.6	-	-

(142)

The concentrations of the reactants are in mol dm<sup>-3</sup>, V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

### Appendix III.28 : Effect of Variation of [Sodium perchlorate] on the rate of oxidation of Galactose at 40°C

Time ↓ (min)	[NaClO <sub>4</sub> ] × 10 = V (a)	Nil V (b)	0.5 V (c)	1.0 V (d)	1.5 V (e)	2.0 V
0	7.0	7.0	7.0	7.0	7.0	7.0
5	5.7	5.6	5.6	5.6	5.6	5.5
10	5.1	5.1	5.0	5.0	5.1	5.0
15	4.2	4.1	4.2	4.1	4.1	4.0
20	3.7	3.6	3.6	3.6	3.6	3.5
25	3.0	3.0	3.1	3.1	2.9	2.8
30	2.7	2.7	2.6	2.6	2.5	2.5
35	2.3	2.4	2.2	2.2	2.1	2.1
40	1.9	1.8	1.7	1.6	1.4	1.4

(143)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

**Appendix III.29 : Effect of Variation of [Sodium perchlorate] on the rate of oxidation of Maltose at 40°C**

Time ↓ (min)	[NaClO <sub>4</sub> ] × 10 = V (a)	NiI V (b)	0.5 V (c)	1.0 V (d)	1.5 V (e)	2.0 V
0	7.0	7.0	7.0	7.0	7.0	7.0
5	6.0	6.1	6.0	5.9	5.9	5.8
10	5.2	5.1	5.	5.0	5.0	4.9
15	4.4	4.4	4.3	4.3	4.3	4.2
20	3.9	3.8	3.8	3.8	3.7	3.7
25	3.3	3.3	3.2	3.2	3.2	3.1
30	2.7	2.7	2.6	2.6	2.5	2.5
35	2.4	2.3	2.3	2.3	2.2	2.1
40	2.0	2.0	1.9	1.9	1.8	1.8
45	-	-	1.7	1.7	1.5	1.4
50	1.5	1.4	-	-	-	-

(144)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture.(min)

### Appendix III.30 : Effect of Variation of [Sodium perchlorate] on the rate of oxidation of Maltose at 40°C

		[IO <sub>4</sub> <sup>-</sup> ] = 2.0x10 <sup>-3</sup> , [S]=0.2x10 <sup>-2</sup> , [OH <sup>-</sup> ]=0.1, [RuCl <sub>3</sub> ]= 3.0x10 <sup>-4</sup> , and [Hypo] = 1.0x10 <sup>-2</sup>						
Time ↓ (min)	[NaClO <sub>4</sub> ] x 10 =	Nil	0.5	1.0	1.5	2.0		
	V	V	V	V	V	V		
	(a)	(b)	(c)	(d)	(e)			
0		7.0	7.0	7.0	7.0	7.0		
5		6.3	6.3	6.2	6.1	6.1		
10		5.6	5.6	5.5	5.5	5.4		
15		5.0	5.1	5.0	4.9	4.8		
20		4.4	4.3	4.2	4.2	4.1		
25		3.8	3.8	3.7	3.7	3.6		
30		3.4	3.5	3.3	3.3	3.2		
35		3.0	3.1	2.9	2.8	2.7		
40		2.7	2.6	2.5	2.5	2.4		
45	-	-	2.0	1.9	1.9	1.7		
50	2.1	2.0	1.5	1.4	1.4	1.2		

(145)

The concentrations of the reactants are in mol dm<sup>-3</sup>; V represents volume of hypo (in ml) required for titration of 5ml of reaction mixture (min)

Chapter - IV

***Ruthenium-III***

***Catalysed Oxidation***

***of Amino Alcohols***

# **Oxidation of Aminoalcohols by $\text{IO}_4^-$ in presence of Ruthenium (III)**

## **IV A Introduction:**

The kinetics of oxidation of aminoalcohols containing both amino and alcoholic groups, have not received much attention.

The kinetics of oxidation of triethanolamine by persulphate<sup>1</sup> in aqueous medium and in an inert atmosphyere at 20-35°C have been investigated. The formaldehyde was found to be oxidation product.

The studies on the oxidation of diethanolamine<sup>2</sup> and triethanolamine<sup>3,4</sup> by hexacyanoferrate (III), in aqueous alkaline medium have shown a first order dependence of rate with respect to each oxidant, substrate and alkali. A mechanism involving, formation of an intermediate amine anion has been propsoed.

The kinetics of oxidation diethanolamine by sodium meta perodate has been studied. The order of reaction with respect to substrate and oxidant was unity, while that with respect to  $\text{OH}^-$  was -1. The oxidation of N-ethyl-diethanolamine with hypochlorite<sup>6</sup> in alkaline medium followed a complex kinetics.

Nicolet and Shinn<sup>7</sup> have investigated the oxidation of aminoalcohols buy periodate. The oxidation products were identified as corresponding aldehydes. Further, studies<sup>8</sup> on the oxidation of aminoalcohols by periodic acid have also shown the carbon-carbon and carbon-nitrogen cleavage products.

Oxidation of aminoalcohols by vanadium (V) in aqueous

perchloric acid medium is reported.<sup>9</sup> The rate of oxidation of aminoalcohol is first order with respect to vanadium (V) and the aminoalcohols. In the proposed mechanism, the rate determining step involves the homolytic decomposition of an {substrate—vanadium (V)} complex and hydride ion abstraction from the substrate.

Ruthenium (III) catalysed oxidation of aminoalcohols by hexacyanoferrate (III) in alkaline medium<sup>10,11</sup> has shown a complex kinetics. A second order dependence of rate with respect to hexacyanoferrate (III) was observed. Primary, secondary and tertiary aminoalcohols showed a wide variation of kinetics results.

Ruthenium (III) catalysed oxidation of aminoalcohols by cerium (IV)<sup>12</sup> in acidic medium has also been investigated. The reactions exhibited a zero order dependence of rate with respect to oxidant, first order rate dependence with respect to each of the substrate and catalyst. First order dependence of rate in sulphuric acid was also found in case of primary aminoalcohols. The mechanism involving a free radical process was proposed for the oxidation.

Recently osmium (VIII) catalysed oxidation of aminoalcohols by alkaline—chloramine—T<sup>13</sup> has also been investigated. The reactions followed a complex kinetics. The mechanism involving {Substrate—chloramine—T} and {osmium (VIII)—substrate} complexes has been proposed for the oxidation process.

The oxidation of aminoalcohols by Sodium meta periodate in

acidic medium does not proceed in absence of the catalyst. Therefore it was thought worth while, to investigate oxidation of aminoalcohols by sodium meta periodate in acidic medium in persence of ruthenium (III) which serves as an effective catalyst in acidic media.

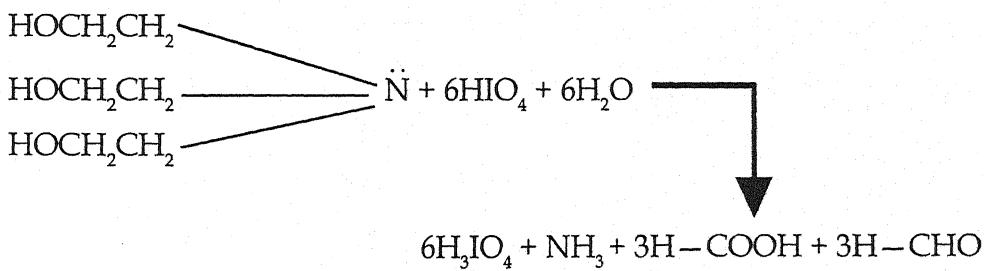
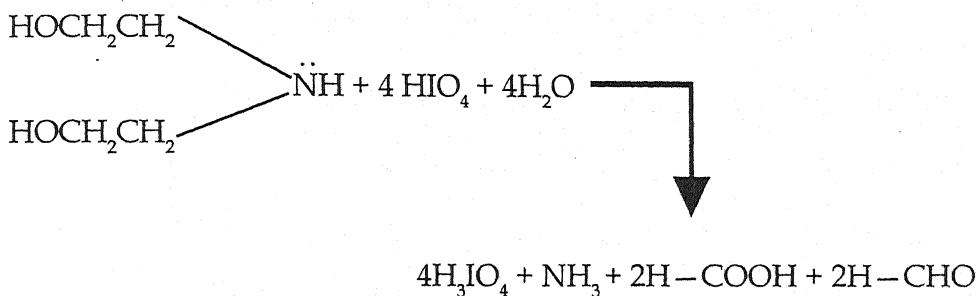
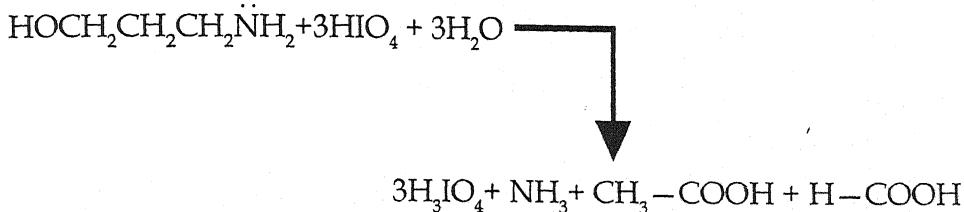
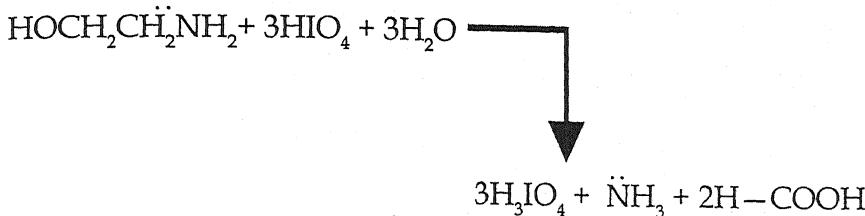
In the present chapter the results of details kinetics of primary aminoalcohols (2 – aminoethanol and 3 – aminopropanol), secondary aminoalcohol (diethanolamine) and tertiary amino alcohol (triethanolamine) by sodium meta periodate in presence of ruthenium (III) chloride, are presented and a suitable mechanism has been proposed for the oxidation process.

## **IV.B. Stoichiometry**

The reaction mixtures containing a known excess of sodium meta periodate in comparison to aminoalcohol were allowed to stand for 72 hours at 40°C in presence of 0.02 M perchloric acid and  $2.4 \times 10^{-4}$  M ruthenium trichloride. Afteer the reaction was complete, the amount of unconsumed sodium meta periodate was estimated iodometrically. The result showed that nearly three mols of sodium meta periodate were consumed for each mol of 2 – amino – ethanol and 3 – aminopropanol whild nearly 4 mols and 6 mols of sodium meta periodate were consumed for each mol of diethanolamine and triethanolamine respectivly.

The results may be represented by following stoichiometric

equations as,



Where 'R' represents  $\text{p}-\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2-$  group.

Carbon–nitrogen cleavage products (formaldehyde and ammonia) resulting from oxidation of amino-alcohols by other oxidants have been reported<sup>8,14</sup>. Formaldehyde and formic acid, as the oxidation products have also been reported during the oxidation of diethanolamine by Sodium meta periodate in alkaline medium.

In the present studies the presence of formic acid (also acetic acid in case of 3 – amino-propanol) as the oxidation product was confirmed by spot tests<sup>15</sup>. It has also been established qualitatively that formaldehyde is oxidised by acidic Sodium meta periodate in presence of ruthenium (III) chloride. Therefore, it is likely that aminoalcohols first give aldehydes as the intermediate products, which are further oxidised to acids in excess of the oxidant.

#### **IV.C Effect of variation in sodium meta periodate concentration.**

In order to determine the dependence of the reaction rate on Sodium meta periodate the kinetic runs were made for oxidation of aminoalcohols at several initial concentration of sodium meta periodate. The concentration of aminoalcohol, ruthenium (III),  $\text{HClO}_4$  were kept constant at  $2.0 \times 10^{-2}$  M,  $2.4 \times 10^{-4}$  M ( $4.8 \times 10^{-4}$  m in case 2 - aminoethanol) and  $2.0 \times 10^{-2}$  M respectively. The amount of hypo required for titration of 5 ml of reaction mixture at different time intervals for various kinetic runs are presented in Tables IV-1, IV-2, IV-3 and IV-4 in case of 2 – aminoethanol, 3 – aminopropanol, diethanolamine and triethanolamine respectively.

It was observed that  $\log (a-x)$  versus time plots were good straight lines upto 80% of the reactions suggesting first order dependence of rate with respect to Sodium meta periodate. Therefore, pseudo – first order rate constants in Sodium meta periodate ( $K_{\text{obs}}$ ) have been evaluated from the slopes of the straight line plotted

between  $\log(a-x)$  versus time. The plots have been shown in Figures IV-C<sub>1</sub> to IV-C<sub>4</sub> for various aminoalcohols. The value of rate constants obtained from the slopes of these straight lines have also been shown in the Tables IV-C<sub>1</sub> to IV-C<sub>4</sub> for each kinetic run.

The values of observed rate constants, at different initial concentration of sodium meta periodate for various aminoalcohols are summarised in Table IV-5. It is clear from the table that observed rate constants remained nearly identical at various initial concentrations of sodium meta periodate in case of each aminoalcohol, which further, confirmed first order dependence of rate with respect to sodium meta periodate.

**Table-IV C-1: Effect in Variation of [Sodium meta periodate] on the Rate of Oxidation of 2-Aminoethanol at 35°C**  
 $(S) = 2.0 \times 10^{-2}M, (HClO_4) = 2.0 \times 10^{-2}M, [Ru(III)] = 4.8 \times 10^{-4}M, (Hypo) = 4.0 \times 10^{-3}M$

Time Minutes	$(CAT) = 1.2 \times 10^{-3}M$		$(CAT) = 1.6 \times 10^{-3}M$		$(CAT) = 2.0 \times 10^{-3}M$		$(CAT) = 2.4 \times 10^{-3}M$		$(CAT) = 3.0 \times 10^{-3}M$	
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	3.5	4.2	5.2	6.0	7.5	-	-	-	-	-
5	3.25	3.8	4.7	5.6	-	-	-	-	-	-
10	2.95	3.35	4.2	5.0	-	-	-	-	-	-
20	2.6	3.2	3.9	4.7	-	-	-	-	-	-
30	2.4	2.8	3.6	4.2	-	-	-	-	-	-
40	1.95	2.35	3.2	3.8	-	-	-	-	-	-
60	1.5	1.95	2.6	3.2	-	-	-	-	-	-
90	1.15	1.35	1.85	2.5	-	-	-	-	-	-
120	-	-	1.5	1.9	-	-	-	-	-	-
150	-	-	-	-	-	-	-	-	-	1.8
$(153)$										1.54
$k_{obs} \times 10^4 \text{ (Sec}^{-1}\text{)}$	1.61	1.63	1.60	1.68						

(Obtained from Plots)

**Table-IV C-2 :Effect in Variation of [Sodium meta periodate] on the Rate of Oxidation of 3-Aminopropanol at 35°C**  
 $(S) = 2.0 \times 10^{-2} M$ ,  $(HClO_4) = 2.0 \times 10^{-2} M$ ,  $[Ru(III)] = 2.4 \times 10^{-4} M$ ,  $(Hypo) = 4.0 \times 10^{-3} M$

Time Minutes	$(CAT) = 1.2 \times 10^{-3} M$		$(CAT) = 1.6 \times 10^{-3} M$		$(CAT) = 2.0 \times 10^{-3} M$		$(CAT) = 2.4 \times 10^{-3} M$		$(CAT) = 3.0 \times 10^{-3} M$	
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	3.9	4.3	4.8	5.25	5.6					
10	3.5	3.8	4.25	4.85						5.2
20	3.25	3.45	4.0	4.5						4.9
30	3.05	3.25	3.7	4.25						4.7
40	2.7	3.1	3.5	4.0						4.4
60	2.45	2.75	3.2	3.6						4.0
90	2.15	2.3	2.6	3.0						3.6
120	1.6	1.9	2.25	2.6						3.1
150	1.4	1.6	2.1	2.2						2.75
										0.86
	$k_{obs} \times 10^4 \text{ (Sec}^{-1}\text{)}$	0.83	0.88	0.85						

(154)

(Obtained from Plots)

**Table-IV C-3: Effect in Variation of [Sodium meta periodate] on the Rate of Oxidation of Diethanolamine at 35°C**  
 $(S) = 2.0 \times 10^{-2} M$ ,  $(HClO_4) = 2.0 \times 10^{-2} M$ ,  $[Ru(III)] = 2.4 \times 10^{-4} M$ ,  $(Hypo) = 4.0 \times 10^{-3} M$

Time Minutes	$(CAT) = 1.2 \times 10^{-3} M$		$(CAT) = 1.6 \times 10^{-3} M$		$(CAT) = 2.0 \times 10^{-3} M$		$(CAT) = 2.4 \times 10^{-3} M$	
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	3.1		4.0		4.45		4.7	
5	2.85		3.75		4.25		4.5	
15	2.7		3.4		3.9		4.2	
25	2.4		3.1		3.65		3.85	
40	2.1		2.75		3.25		3.6	
60	1.85		2.4		2.75		3.1	
90	1.45		1.9		2.2		2.5	
120	1.2		1.6		1.8		2.1	
150	-		1.3		1.5		1.8	
$\bar{K}_{obs} \times 10^4$ (Sec $^{-1}$ )	1.24		1.30		1.20		1.34	

(Obtained from Plots)

**Table-IV C-4 :Effect in Variation of [Sodium meta periodate] on the Rate of Oxidation of 2-Aminoethanol at 35°C**  
 $(S) = 2.0 \times 10^{-2}M, (HClO_4) = 2.0 \times 10^{-2}M, [Ru(III)] = 4.8 \times 10^{-4}M, (Hypo) = 4.0 \times 10^{-3}M$

Time Minutes	(CAT) = 1.2x10 <sup>-3</sup> M		(CAT) = 1.6x10 <sup>-3</sup> M		(CAT) = 2.0x10 <sup>-3</sup> M		(CAT) = 2.4x10 <sup>-3</sup> M	
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	3.8		4.3		5.1		5.7	
5	3.25		4.0		4.5		5.2	
10	3.0	-	-	-	-	-	-	-
15	2.7		3.6		4.1		4.8	
25	2.3		3.0		3.7		4.4	
35	2.0		-	-	-	-	-	-
45	1.7		2.5		3.1		3.9	
60	1.4		2.15		2.7		3.4	
90	-		1.6		2.2		2.9	
120	-		1.3		1.65		2.2	
150	-		-	-	1.25		1.8	
$k_{obs} \times 10^4$ (Sec <sup>-1</sup> )	1.91		1.43		1.50		1.24	

(156)

(Obtained from Plots)

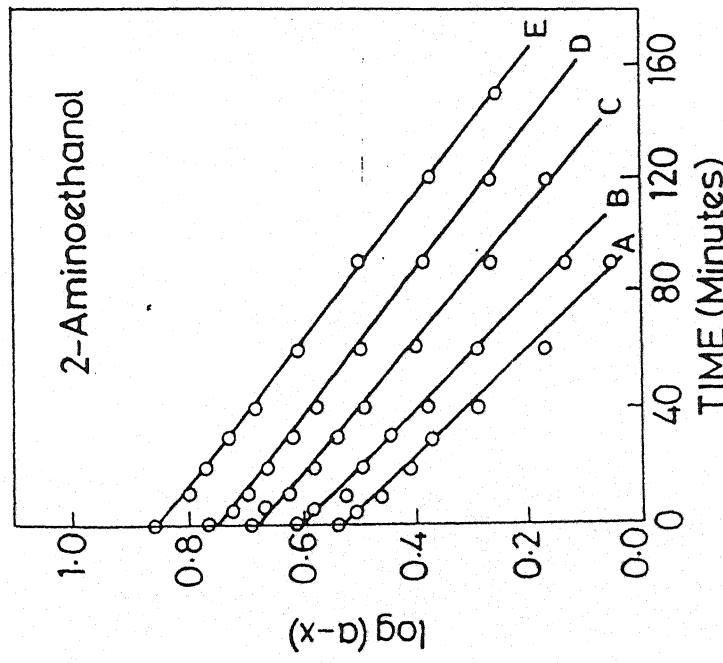


Fig. -IV C-1 First order rate plots at 35°C  
 $[S] = 2.0 \times 10^{-2} M$ ,  $(\text{HIO}_4) = 2.0 \times 10^{-2} M$ ,  
 $[\text{Ru(III)}] = 4.8 \times 10^{-4} M$ ,  $[\text{CAT}] = 1.2, 1.6, 2.0,$   
 $2.4$  and  $3.0 \times 10^{-3} M$  for A, B, C, D and E

respectively

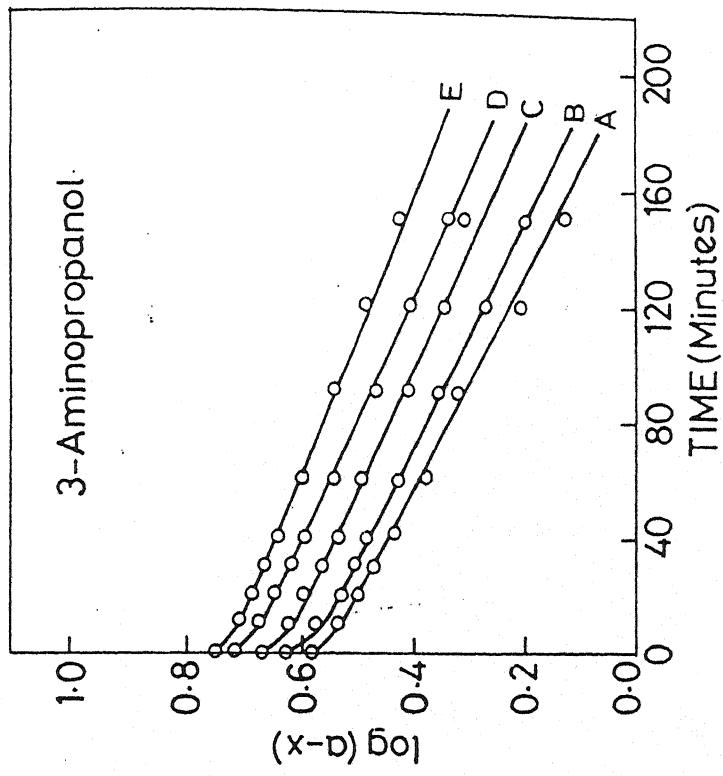


Fig. -IV C-2 First order rate plots at 35°C  
 $[S] = 2.0 \times 10^{-2} M$ ,  $(\text{HIO}_4) = 2.0 \times 10^{-2} M$ ,  
 $[\text{Ru(III)}] = 4.8 \times 10^{-4} M$ ,  $[\text{CAT}] = 1.2, 1.6, 2.0,$   
 $2.4$  and  $3.0 \times 10^{-3} M$  for A, B, C, D and E

respectively

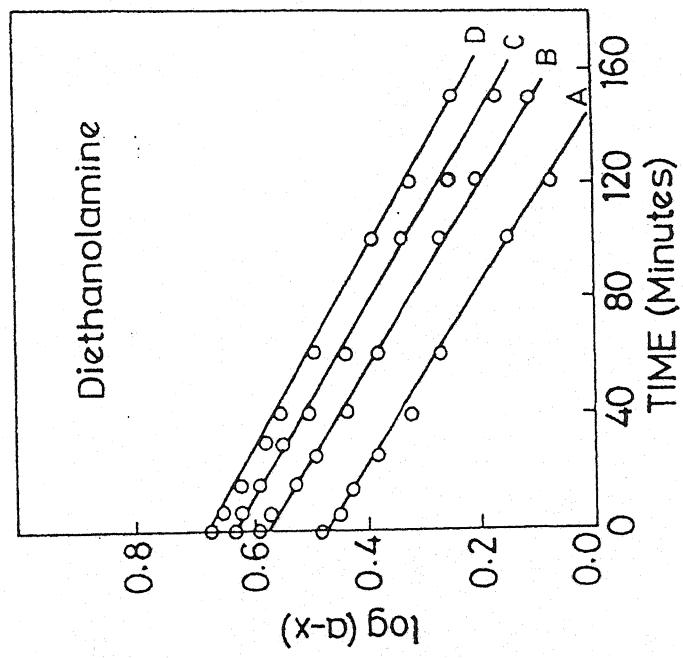


Fig. 4.3 First order rate plots at 35°C  
 $[S] = 2.0 \times 10^{-2} M$ ,  $(\text{HIO}_4) = 2.0 \times 10^{-2} M$ ,  
 $[\text{Ru(III)}] = 4.8 \times 10^{-4} M$ ,  $[\text{CAT}] = 1.2, 1.6, 2.0$ ,  
and  $2.4 \times 10^{-3} M$  for A, B, C and D  
respectively

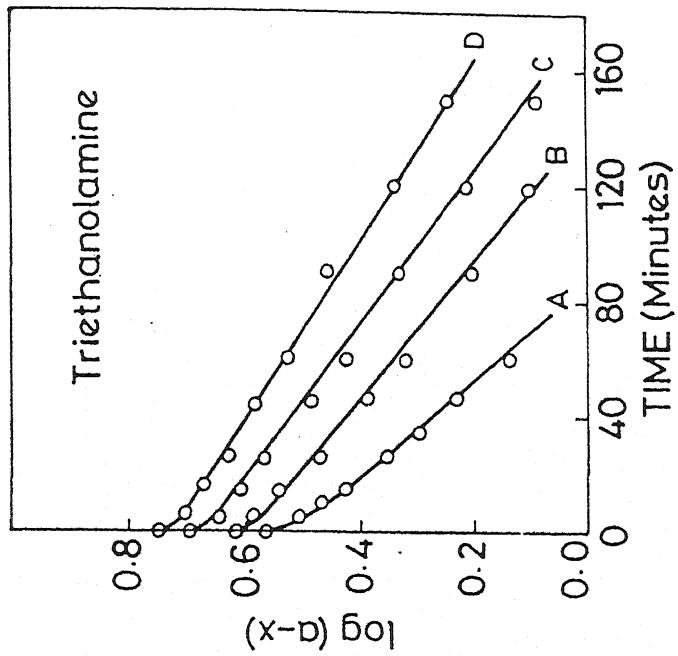


Fig. 4.4 First order rate plots at 35°C  
 $[S] = 2.0 \times 10^{-2} M$ ,  $(\text{HIO}_4) = 2.0 \times 10^{-2} M$ ,  
 $[\text{Ru(III)}] = 4.8 \times 10^{-4} M$ ,  $[\text{CAT}] = 1.2, 1.6, 2.0$ ,  
and  $2.4 \times 10^{-3} M$  for A, B, C and D  
respectively

**Table-IV C-5 : Effect of [Sodium meta periodate] on the Rate Constants at 35°C**

Sodium meta periodate	$k_{obs.} \times 10^4 \text{ sec}^{-1}$	2-Aminoethanol	3-Aminopropanol	Diethanolamine	Triethanolamine
1.2	1.61		0.83	1.25	1.91
1.6	1.63		0.83	1.30	1.43
2.0	1.60		0.88	1.20	1.50
2.4	1.68		0.85	1.34	1.24
3.0	1.54		0.86	-	-

(159)

$[\text{HIO}_4] = 2.0 \times 10^{-2}\text{M}$ ;  $[\text{Aminoalcohol}] = 2.0 \times 10^{-2}\text{M}$  and  $[\text{RuCl}_3] = 2.4 \times 10^{-4}\text{M}$  for 3—Aminopropanol. Diethanolamine, Triethanolamine and  $4.8 \times 10^4\text{M}$  for 2—Aminoethanol.

## **IV D Effect of variation in aminoalcohol Concentrations**

To determine the order of reaction in aminoalcohols, the oxidation kinetics were investigated at several initial concentrations of aminoalcohols under isolating conditions (Aminoalcohol)  $\gg$  [(CAT)] and at a constant concentration of sodium meta periodate ( $2.0 \times 10^{-3}$  M), ruthenium (III) ( $4.8 \times 10^{-4}$  M in case of 2-aminoethanol and  $2.4 \times 10^{-4}$  M in other cases) perchloric acid ( $2.0 \times 10^{-2}$  M). The results are presented in Tables IV D-1, IV D-2, IV D-3 and IV D-4 for the oxidation of 2-aminoethanol, 3-aminopropanol, diethanolamine and triethanolamine respectively and represented graphically in Figures IV D-1 to IV D-4.

The rate constants at different initial concentrations of aminoalcohols are summarised in Table IV D-5, which shows that an increase in the initial concentration of aminoalcohols resulted in a negligible effect on the rate constants. It, therefore, appears that order of reaction in aminoalcohols is zero.

## **IV E Effect of variation in Ruthenium (III) concentration**

The rates of oxidation of aminoalcohols by Sodium meta periodate in acidic medium were found to be strongly dependent on the catalyst ruthenium (III). Measurements were made at various ruthenium (III) chloride concentrations keeping concentration of Sodium meta periodate, aminoalcohol and  $\text{HClO}_4$  as  $2.0 \times 10^{-3}$  M,

**Table-IV D-1: Effect in Variation of [2-Aminoethanol] on the Rate of Oxidation at 35°C (CAT) =  $2.0 \times 10^{-3} M$ ,  $(HClO_4) = 2.0 \times 10^{-2} M$ , (Ru (III)) =  $4.8 \times 10^{-4} M$ , (Hypo) =  $4.0 \times 10^{-3} M$**

Time Minutes	Vol. of Hypo used ml.	$(S) = 1.6 \times 10^{-2} M$		$(S) = 2.0 \times 10^{-2} M$		$(S) = 3.0 \times 10^{-2} M$		$(S) = 4.0 \times 10^{-2} M$	
		Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0		5.2		5.2		5.2		5.2	
5		4.9		4.8		4.7		4.4	
10		4.7		4.5		4.2		3.9	
20		4.5		4.2		3.9		3.7	
30		4.1		3.8		3.6		3.35	
40		3.7		3.5		3.2		3.0	
60		3.25		3.0		2.6		2.4	
90		2.65		2.35		1.85		1.7	
120		2.2		1.9		1.5		1.35	
$k_{obs} \times 10^4$ (Sec <sup>-1</sup> )	1.18		1.20		1.60		1.72		1.80

(161)

(Obtained from Plots)

**Table-IV D-2: Effect in Variation of [3-Aminoproponol] on the Rate of Oxidation at 35°C (CAT) =  $2.0 \times 10^{-3} M$ ,  
 $(HClO_4) = 2.0 \times 10^{-2} M$ , (Ru (III)) =  $2.4 \times 10^{-4} M$ ,  
 $(Hypo) = 4.0 \times 10^{-3} M$**

Time Minutes	$(S) = 1.2 \times 10^{-2} M$		$(S) = 1.6 \times 10^{-2} M$		$(S) = 2.0 \times 10^{-2} M$		$(S) = 3.0 \times 10^{-2} M$		$(S) = 4.0 \times 10^{-2} M$	
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	5.2	5.2	4.8	4.8	5.2	5.2	5.15	5.15	5.15	5.15
10	4.7	4.5	4.3	4.3	4.1	4.1	3.8	3.8	3.8	3.8
20	4.5	4.2	4.0	4.0	3.9	3.9	3.6	3.6	3.6	3.6
30	4.3	4.0	3.7	3.7	3.6	3.6	3.3	3.3	3.3	3.3
40	4.15	3.9	3.5	3.5	3.2	3.2	2.9	2.9	2.9	2.9
60	3.8	3.7	3.2	3.2	2.6	2.6	2.5	2.5	2.5	2.5
90	3.5	3.2	2.6	2.6	2.1	2.1	1.9	1.9	1.9	1.9
120	3.1	2.85	2.25	2.25	1.8	1.8	1.6	1.6	1.6	1.6
150	2.7	2.4	2.1	2.1	1.8	1.8	0.92	0.92	0.92	0.92
$K_{obs} \times 10^4$ (Sec $^{-1}$ )	0.70	0.76	0.88	0.88	0.92	0.92	0.96	0.96	0.96	0.96

(162)

(Obtained from Plots)

**Table-IV D-3: Effect in Variation of [Diethanolamine] on the Rate of Oxidation at 35°C (CAT) =  $2.0 \times 10^{-3}$  M,  $(\text{HClO}_4) = 2.0 \times 10^{-2}$  M,  $(\text{Ru (III)}) = 2.4 \times 10^{-4}$  M,  $(\text{Hypo}) = 4.0 \times 10^{-3}$  M**

Minutes	$(S) = 1.2 \times 10^{-2}$ M		$(S) = 1.6 \times 10^{-2}$ M		$(S) = 2.0 \times 10^{-2}$ M		$(S) = 3.0 \times 10^{-3}$ M		$(S) = 4.0 \times 10^{-3}$ M	
	Time	Vol. of Hypo used	Vol. of Hypo used	Vol. of Hypo used	Vol. of Hypo used	Vol. of Hypo used	Vol. of Hypo used	Vol. of Hypo used	Vol. of Hypo used	Vol. of Hypo used
0		4.6	4.6	4.45	4.6	4.6	4.6	4.6	4.6	4.6
5		4.4	4.3	4.25	4.1	4.1	4.0	4.0	4.0	4.0
15		4.3	4.15	3.9	3.7	3.7	3.55	3.55	3.55	3.55
25		4.1	3.95	3.65	3.4	3.4	3.2	3.2	3.2	3.2
40		3.75	3.7	3.25	2.9	2.9	2.7	2.7	2.7	2.7
60		3.35	3.3	2.75	2.6	2.6	2.4	2.4	2.4	2.4
90		2.85	2.8	2.2	2.1	2.1	1.8	1.8	1.8	1.8
120		2.4	2.25	1.8	1.6	1.6	1.3	1.3	1.3	1.3
150		2.1	1.8	1.5	1.35	1.35	1.0	1.0	1.0	1.0
$k_{\text{obs}} \times 10^4$ (Sec <sup>-1</sup> )		1.15	1.26	1.20	1.34	1.34	1.53	1.53	1.53	1.53

(Obtained from Plots)

**Table-IV D-4: Effect in Variation of [Triethanolamine] on the Rate of Oxidation at 35°C (CAT) =  $2.0 \times 10^{-3}$ M,  $(\text{HClO}_4) = 2.0 \times 10^{-2}$ M, (Ru (III)) =  $2.4 \times 10^{-4}$ M, (Hypo) =  $4.0 \times 10^{-3}$ M**

Time Minutes	$(S) = 1.2 \times 10^{-2}$ M		$(S) = 1.6 \times 10^{-2}$ M		$(S) = 2.0 \times 10^{-2}$ M		$(S) = 3.0 \times 10^{-2}$ M		$(S) = 4.0 \times 10^{-2}$ M	
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	5.2	5.2	5.1	5.1	5.2	5.2	5.2	5.2	5.2	5.2
5	5.0	4.7	4.5	4.5	4.3	4.3	4.3	4.0	4.0	4.0
15	4.55	4.3	4.1	4.1	3.9	3.9	3.9	3.7	3.7	3.7
25	4.0	3.9	3.7	3.7	3.6	3.6	3.6	3.4	3.4	3.0
45	3.7	3.4	3.1	3.1	2.9	2.9	2.7	2.7	2.7	2.5
60	3.0	2.9	2.7	2.7	2.5	2.5	2.2	2.2	2.2	1.9
90	2.5	2.25	2.2	2.2	2.0	2.0	1.7	1.7	1.7	1.4
120	1.95	1.8	1.65	1.65	1.4	1.4	1.25	1.25	1.25	-
150	1.5	1.4	1.25	1.25	-	-	-	-	-	-
$k_{\text{obs}} \times 10^4$ (Sec $^{-1}$ )	1.34	1.35	1.50	1.50	1.72	1.72	1.72	1.72	1.72	1.91

(164)

(Obtained from Plots)

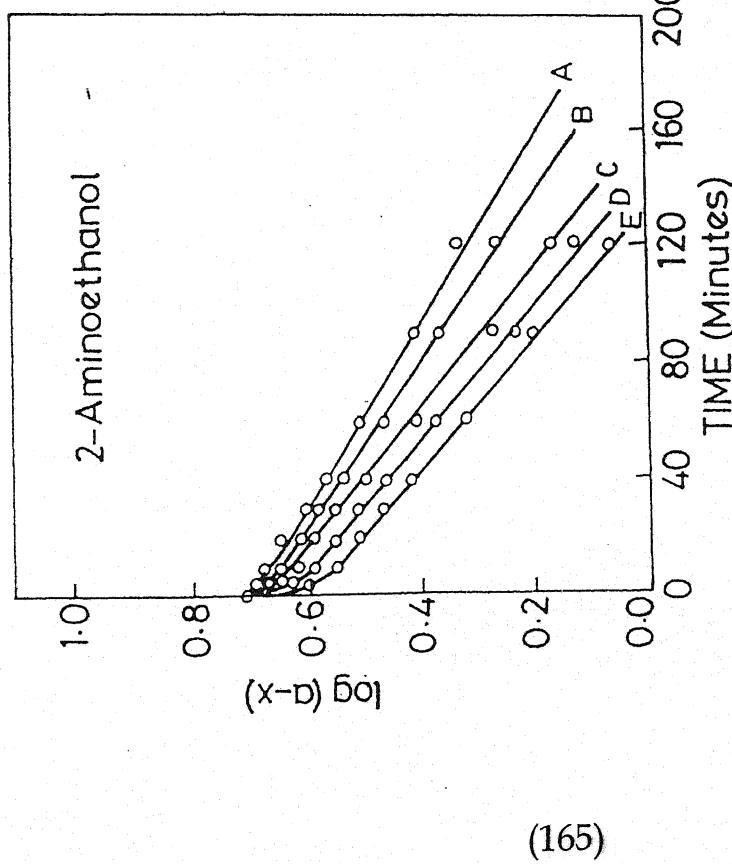


Fig.-IV D-1: First order rate plots at 35°C  
 $[CAT]=2.0 \times 10^{-3}M$ ,  $[HClO_4]=2.0 \times 10^{-2}M$ ,  
 $[Ru(III)]=4.8 \times 10^{-4}M$ ,  $[S]=1.2, 1.6, 2.0, 3.0$   
 and  $4.0 \times 10^{-2}M$  for A, B, C, D and E  
 respectively

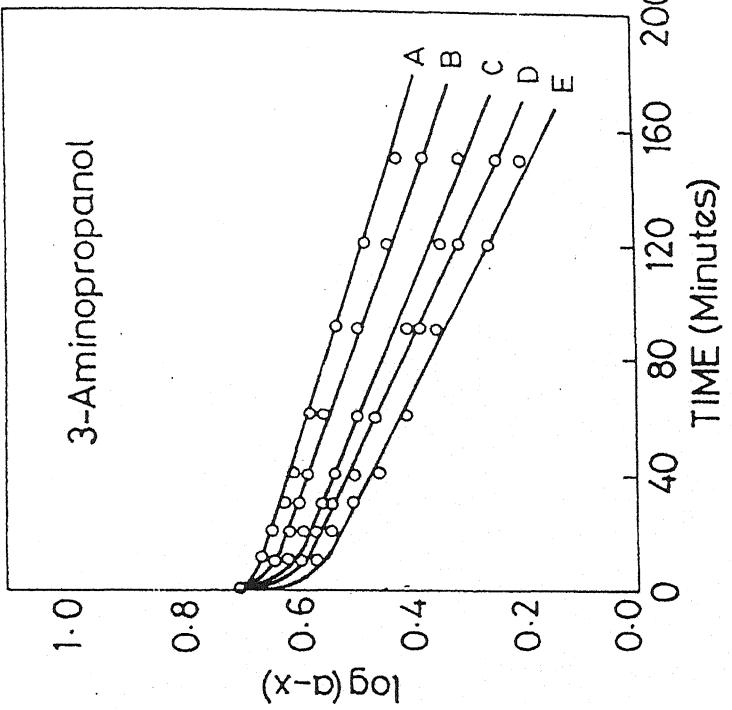


Fig.-IV D-2: First order rate plots at 35°C  
 $[CAT]=2.0 \times 10^{-3}M$ ,  $[HClO_4]=2.0 \times 10^{-2}M$ ,  
 $[Ru(III)]=2.4 \times 10^{-4}M$ ,  $[S]=1.2, 1.6, 2.0, 3.0$   
 and  $4.0 \times 10^{-2}M$  for A, B, C, D and E  
 respectively

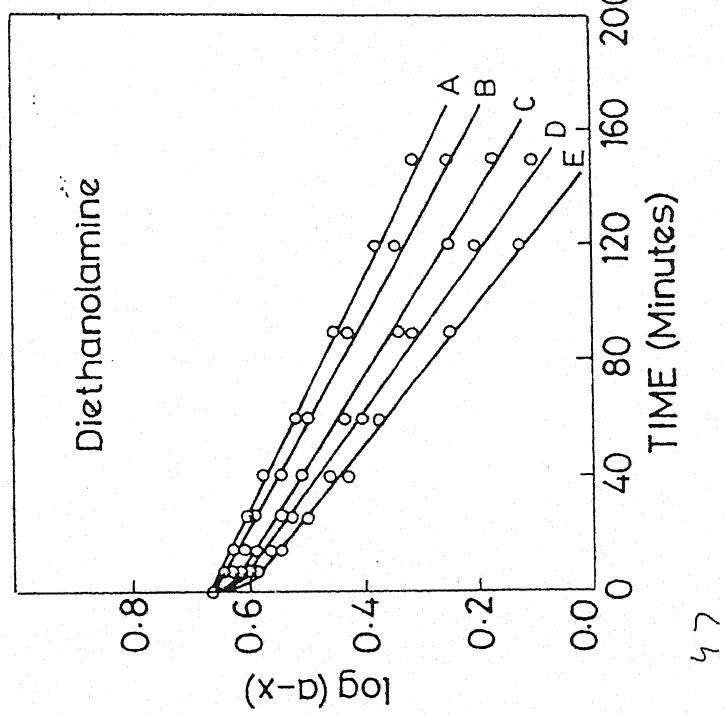


Fig.-IV D-3: First order rate plots at 35°C  
 $[CAT] = 2.0 \times 10^{-3} M$ ,  $[HClO_4] = 2.0 \times 10^{-2} M$ ,  
 $[Ru(III)] = 2.4 \times 10^{-4} M$ ,  $[S] = 1.2, 1.6, 2.0, 3.0$   
 and  $4.0 \times 10^{-2} M$  for A, B, C, D and E  
 respectively

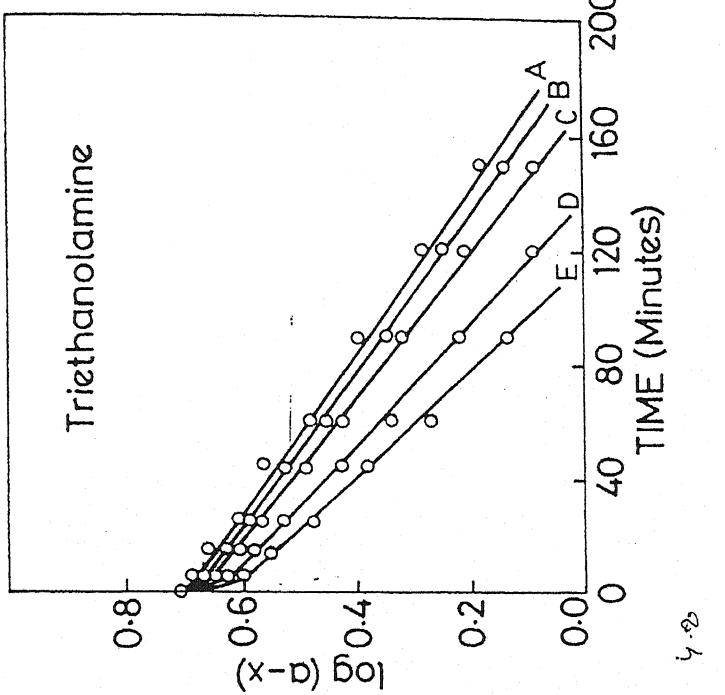


Fig.-IV D-4: First order rate plots at 35°C  
 $[CAT] = 2.0 \times 10^{-3} M$ ,  $[HClO_4] = 2.0 \times 10^{-2} M$ ,  
 $[Ru(III)] = 2.4 \times 10^{-4} M$ ,  $[S] = 1.2, 1.6, 2.0, 3.0$   
 and  $4.0 \times 10^{-2} M$  for A, B, C, D and E  
 respectively

**Table-IV D-5: Effect of [Aminoalcohol] on the Rate Constants at 35°C**

Aminoalcohol	$10^2 M$	$2 - \text{Aminoethanol}$	$3 - \text{Aminopropanol}$	$3 - \text{Diethanolamine}$	$\text{Triethanolamine}$
	1.2	1.18	0.70	1.15	1.34
	1.6	1.20	0.76	1.26	1.35
	2.0	1.60	0.88	1.20	1.50
	3.0	1.72	0.92	1.34	1.72
	4.0	1.80	0.96	1.53	1.91

(167)

Sodium meta periodate  $2.0 \times 10^{-3} M$ ;  $[\text{HClO}_4] = 2.0 \times 10^{-2} M$  and  $[\text{RuCl}_3] = 2.4 \times 10^{-4} M$  for 3—Aminopropanol. Diethanolamine, Triethanolamine and  $4.8 \times 10^4 M$  for 2—Aminoethanol.

$2.0 \times 10^{-3} \text{M}$  and  $2.0 \times 10^{-2} \text{M}$  respectively. The results are tabulated in Tables IV E -1 to IV E-4 and represented graphically in Figures IV E-1 to IV E-4.

The results of the effect of ruthenium (III) Concentration on the rate constants for oxidation of various aminoalcohols may be summarised in Table IV E-5. It is evident from the table that an increase in ruthenium (III) concentration proportionally increases the observed pseudo-first rate constant with respect to sodium meta periodate. The plots of  $k_{\text{obs}}$ . versus [Ruthenium (III)] (figures IV E-5) represent straight lines passing through origin. The reaction is, therefore, of first order with respect to ruthenium (III) concentration.

## **IV-F Effect of variation in perchloric acid concentration**

In order to a certain the dependence of the rate on  $\text{HClO}_4$  concentration, the kinetics were followed at several initial concentrations of perchloric acid and at a fixed ionic strength. The concentrations of aminoalcohol, ruthenium (III) and sodium meta periodate were kept constant at  $2.0 \times 10^{-2} \text{M}$ ,  $2.4 \times 10^{-4} \text{M}$  ( $4.8 \times 10^{-4} \text{M}$  in case of 2-aminoethanol) and  $2.0 \times 10^{-3} \text{M}$  respectively and the total ionic strength was fixed at  $0.04 \text{M}$  by adding different amount of  $\text{NaClO}_4$ . The amount of acid already present in the catalyst was taken into consideration. The results are presented in Tables IV F-1 to IV F-4 and represented graphically in Figures IV F-1 to IV F-4. The results of acid concentration of the rate of oxidation of various

**Table-IV E-1: Effect in Variation of [Ruthenium (III)] on the Rate of Oxidation of 2-Aminoethanol at 35°C**  
 $(S) = 2.0 \times 10^{-2} M$ , (CAT) =  $2.0 \times 10^{-3} M$ ,  
 $(\text{HIO}_4) = 2.0 \times 10^{-2} M$ , (Hypo) =  $4.0 \times 10^{-3} M$

Time Minutes	$[\text{Ru(III)}] = 2.4 \times 10^{-4} M$		$[\text{Ru(III)}] = 3.6 \times 10^{-4} M$		$[\text{Ru(III)}] = 4.8 \times 10^{-4} M$		$[\text{Ru(III)}] = 7.2 \times 10^{-4} M$		$[\text{Ru(III)}] = 9.6 \times 10^{-4} M$	
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	5.2		5.2		5.2		5.1		5.1	
5	5.0		4.9		4.7		4.6		4.4	
10	4.8		4.6		4.2		4.1		3.9	
20	4.4		4.25		3.9		3.7		3.5	
30	4.0		3.8		3.6		3.35		3.0	
40	3.8		3.5		3.2		3.0		2.5	
60	3.4		3.0		2.6		2.3		1.8	
90	3.0		2.5		1.85		1.6		-	
120	2.5		2.0		1.5		-		-	
150	-		-		-		-		-	
$K_{\text{obs}} \times 10^4 \text{ (Sec}^{-1}\text{)}$	0.76		1.15		1.61		1.91		3.05	

(169)

(Obtained from Plots)

**Table-IV E-2 : Effect in Variation of [Ruthenium (III)] on the Rate of Oxidation of 3-Aminoproponol at 35°C**  
 $(S) = 2.0 \times 10^{-2} M$ , (CAT) =  $2.0 \times 10^{-3} M$ ,  
 $(\text{HIO}_4) = 2.0 \times 10^{-2} M$ , (Hypo) =  $4.0 \times 10^{-3} M$

Time Minutes	$[\text{Ru(III)}] = 1.2 \times 10^{-4} M$		$[\text{Ru(III)}] = 1.9 \times 10^{-4} M$		$[\text{Ru(III)}] = 2.4 \times 10^{-4} M$		$[\text{Ru(III)}] = 3.6 \times 10^{-4} M$		$[\text{Ru(III)}] = 4.8 \times 10^{-4} M$	
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	4.75		4.75		4.8		4.75		4.75	
10	4.55		4.45		4.25		4.15		3.8	
20	4.3		4.2		4.0		3.8		3.6	
30	4.15		4.0		3.7		3.6		3.3	
40	3.8		3.6		3.5		3.2		3.0	
60	3.6		3.35		3.2		2.85		2.5	
90	3.2		2.75		2.6		2.3		1.8	
120	2.85		2.35		2.25		1.85		1.35	
150	2.6		2.25		2.1		1.45		-	
	$k_{\text{obs.}} \times 10^4 \text{ (Sec}^{-1}\text{)}$	0.46		0.76		0.88		1.33		1.73

(170)

(Obtained from Plots)

**Table-IV E-3 : Effect in Variation of [Ruthenium (III)] on the Rate of Oxidation of Diethanolamine at 35°C**  
 $(S) = 2.0 \times 10^{-2} M$ ,  $(CAT) = 2.0 \times 10^{-3} M$ ,  
 $(HIO_4) = 2.0 \times 10^{-2} M$ ,  $(Hypo) = 4.0 \times 10^{-3} M$

Time (171)	$[Ru(III)] = 1.2 \times 10^{-4} M$		$[Ru(III)] = 1.9 \times 10^{-4} M$		$[Ru(III)] = 2.4 \times 10^{-4} M$		$[Ru(III)] = 3.6 \times 10^{-4} M$		$[Ru(III)] = 4.8 \times 10^{-4} M$	
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	4.6	4.6	4.6	4.45	4.45	4.55	4.55	4.55	4.5	4.5
5	4.35	4.3	4.3	4.25	4.25	4.0	4.0	4.0	3.85	3.85
15	4.1	4.0	4.0	3.9	3.9	3.7	3.7	3.7	3.4	3.4
25	3.85	3.7	3.7	3.65	3.65	3.25	3.25	3.25	2.85	2.85
40	3.55	3.35	3.35	3.25	3.25	2.75	2.75	2.75	2.35	2.35
60	3.25	3.0	3.0	2.75	2.75	2.3	2.3	2.3	1.85	1.85
90	2.9	2.6	2.6	2.2	2.2	1.75	1.75	1.75	1.25	1.25
120	2.7	2.3	2.3	1.8	1.8	1.35	1.35	1.35	-	-
150	2.4	1.9	1.9	1.5	1.5	-	-	-	-	-
$K_{obs} \times 10^4$ (Sec <sup>-1</sup> )	0.58	0.96	1.20	1.72	1.72	2.49	2.49	2.49		

(Obtained from Plots)

**Table-IV E-4 : Effect in Variation of [Ruthenium (III)] on the Rate of Oxidation of Triethanolamine at 35°C**  
 $(S) = 2.0 \times 10^{-2} M$ , (CAT) =  $2.0 \times 10^{-3} M$ ,  
 $(\text{HIO}_4) = 2.0 \times 10^{-2} M$ , (Hypo) =  $4.0 \times 10^{-3} M$

Time Minutes	$[\text{Ru(III)}] = 1.2 \times 10^{-4} M$		$[\text{Ru(III)}] = 1.9 \times 10^{-4} M$		$[\text{Ru(III)}] = 2.4 \times 10^{-4} M$		$[\text{Ru(III)}] = 3.6 \times 10^{-4} M$		$[\text{Ru(III)}] = 4.8 \times 10^{-4} M$	
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	5.2		5.2		5.1		5.2		5.2	
5	4.85		4.7		4.5		4.3		4.0	
15	4.65		4.3		4.1		3.7		3.35	
25	4.25		3.9		3.7		3.15		2.7	
45	3.8		3.45		3.1		2.5		2.2	
60	3.45		3.05		2.7		2.2		1.8	
90	3.15		2.5		2.2		1.55		1.2	
120	2.65		2.1		1.65		1.2		-	
150	2.25		1.8		1.25		-		-	
$k_{\text{obs}} \times 10^4 \text{ (Sec}^{-1}\text{)}$		0.67		1.15		1.50		1.92		2.87

(Obtained from Plots)

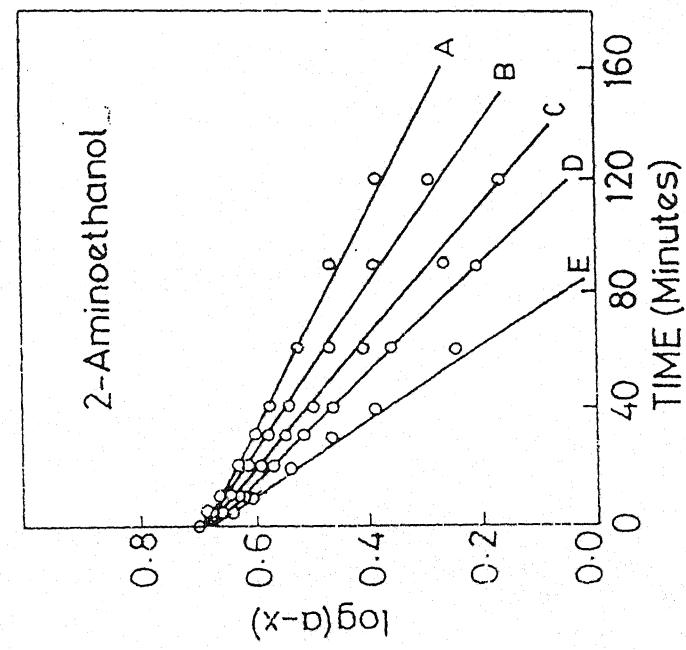


Fig.-IV E-1 First order rate plots at 35°C  
 $[S] = 2.0 \times 10^{-2} M$  [CAT] =  $2.0 \times 10^{-3} M$ ,  
 $[\text{HIO}_4] = 2.0 \times 10^{-2} M$ ,  $[\text{Ru(III)}] = 2.4, 3.6, 4.8,$   
 $7.2$  and  $9.6 \times 10^{-4} M$  for A, B, C, D and E  
respectively

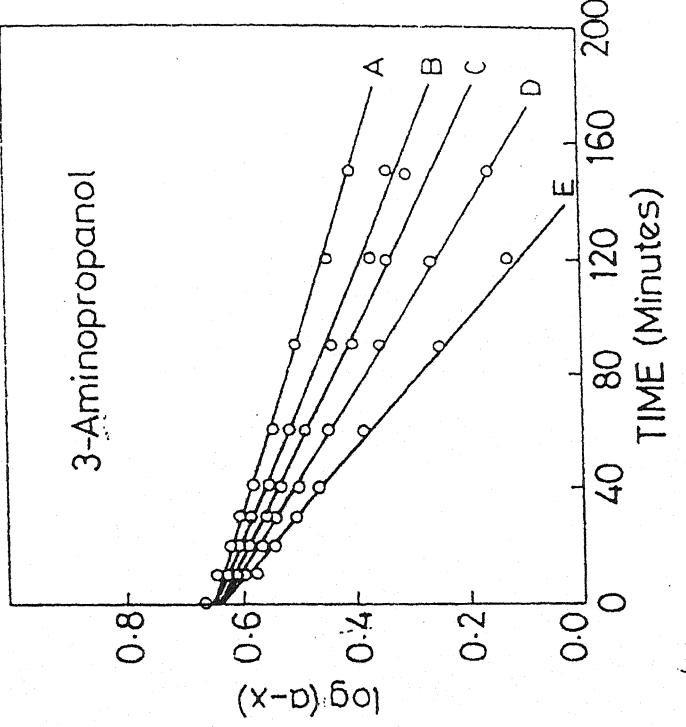
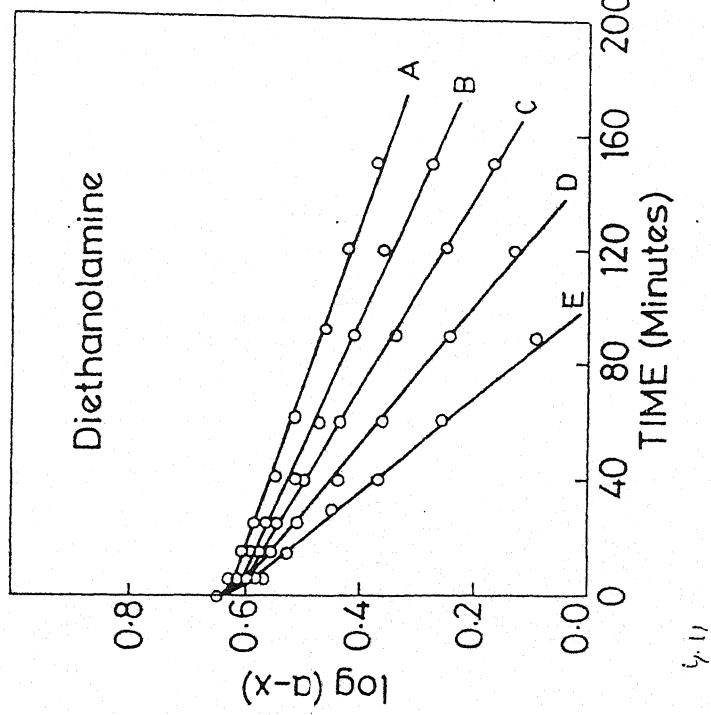


Fig.-IV E-2 First order rate plots at 35°C  
 $[S] = 2.0 \times 10^{-2} M$  [CAT] =  $2.0 \times 10^{-3} M$ ,  
 $[\text{HIO}_4] = 2.0 \times 10^{-2} M$ ,  $[\text{Ru(III)}] = 1.2, 1.9,$   
 $2.4, 3.6$  and  $4.8 \times 10^{-4} M$  for A, B, C, D and E  
respectively



(174)

Fig.-IV E-3 First order rate plots at  $35^{\circ}\text{C}$   
 $[\text{S}] = 2.0 \times 10^{-2}\text{M}$   $[\text{CAT}] = 2.0 \times 10^{-3}\text{M}$ ,  
 $[\text{HIO}_4] = 2.0 \times 10^{-2}\text{M}$ ,  $[\text{Ru(III)}] = 1.2, 1.9, 2.4,$   
 $3.6$  and  $4.8 \times 10^{-4}\text{M}$  for A, B, C, D and E

respectively

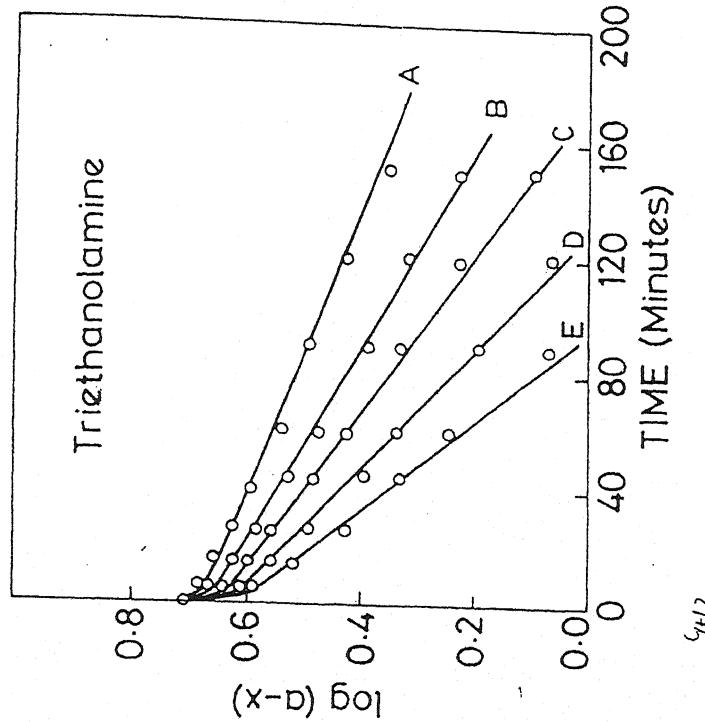


Fig.-IV E-4 First order rate plots at  $35^{\circ}\text{C}$   
 $[\text{S}] = 2.0 \times 10^{-2}\text{M}$   $[\text{CAT}] = 2.0 \times 10^{-3}\text{M}$ ,  
 $[\text{HIO}_4] = 2.0 \times 10^{-2}\text{M}$ ,  $[\text{Ru(III)}] = 1.2, 1.9,$   
 $2.4, 3.6$  and  $4.8 \times 10^{-4}\text{M}$  for A, B, C, D and E

respectively

**Table-IV E-5 : Effect of [Ruthenium (III)] on the Rate Constants  
at 35°C**

[Ru(III)] $10^4 M$	$k_{obs} \times 10^4 \text{ (sec}^{-1}\text{)}$	2 - Aminoethanol	3 - Aminopropanol	Diethanolamine	Triethanolamine
1.2	-		0.46	0.58	0.67
1.9	-		0.76	0.96	1.15
2.4	0.76		0.88	1.20	1.50
3.6	1.15		7.33	1.72	1.92
4.8	1.61		1.73	2.49	2.87
7.2	1.91		-	-	-
9.6	3.05		-	-	-

(175)

Sodium meta periodate  $2.0 \times 10^{-3} M$ ;  $[\text{HClO}_4] = 2.0 \times 10^{-2} M$  and  $[\text{Aminoalcohol}] 2.0 \times 10^{-2} M$

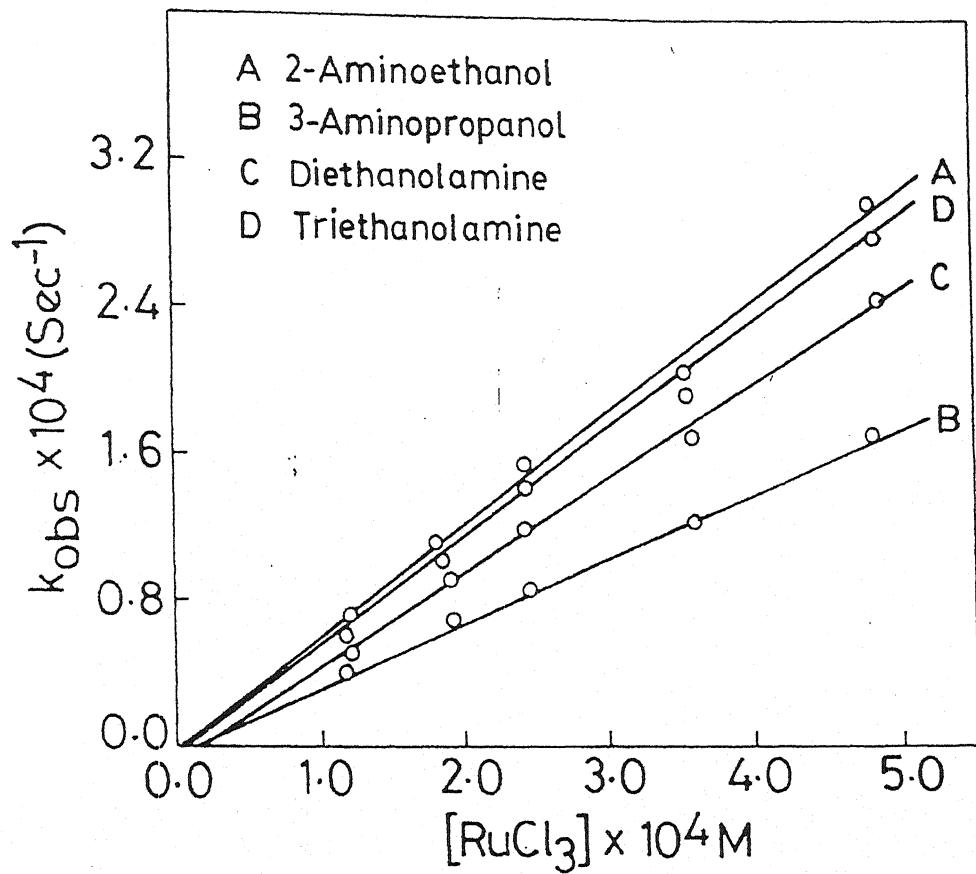


Fig.-IV E-5 Plots of  $K_{obs}$  versus  $[\text{RuCl}_3]$  at  
 $35^\circ\text{C}$   $[\text{S}] = 2.0 \times 10^{-2} \text{ M}$   $[\text{CAT}] = 2.0 \times 10^{-3} \text{ M}$ ,  
 $(\text{HClO}_4) = 2.0 \times 10^{-2} \text{ M}$ .

**Table-IV F-1 : Effect in Variation of [Perchloric Acid] on the Rate of Oxidation of 2-Aminoethanol at 35°C**  
 $(S) = 2.0 \times 10^{-2} M$ , (CAT) =  $2.0 \times 10^{-3} M$ ,  
 $[Ru(III)] = 4.8 \times 10^{-4} M$ , (Hypo) =  $4.0 \times 10^{-3} M$ ,  
 $\mu - 0.04 M$  (Maintained by  $NaClO_4$ )

Time Minutes	$[HClO_4] = 1.2 \times 10^{-2} M$		$[HClO_4] = 1.6 \times 10^{-2} M$		$[HClO_4] = 2.0 \times 10^{-2} M$		$[HClO_4] = 3.0 \times 10^{-2} M$		$[HClO_4] = 4.0 \times 10^{-2} M$	
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	5.15	5.15	5.2	5.2	5.15	5.15	5.15	5.15	5.15	5.15
5	-	4.7	4.7	4.7	-	4.45	-	4.45	-	4.3
10	4.7	4.4	4.4	4.4	4.2	4.1	4.1	4.1	4.1	3.9
20	4.4	4.15	4.15	4.15	3.9	3.7	3.7	3.7	3.7	3.5
30	4.0	3.8	3.8	3.8	3.6	3.4	3.4	3.4	3.4	3.0
40	3.7	3.5	3.5	3.5	3.2	3.0	3.0	3.0	3.0	2.5
60	3.4	3.1	3.1	3.1	2.6	2.3	2.3	2.3	2.3	1.9
90	2.85	2.4	2.4	2.4	1.85	1.6	1.6	1.6	1.6	1.35
120	2.35	1.9	1.9	1.9	1.5	-	-	-	-	-
150	2.0	-	-	-	-	-	-	-	-	-

(177)

$k_{obs} \times 10^4$  (Sec $^{-1}$ ) 0.96

1.33 1.60 1.91 2.12

(Obtained from Plots)

**Table-IV F-2 : Effect in Variation of [Perchloric Acid] on the Rate of Oxidation of 2-Aminopropanol at 35°C**  
 $(S) = 2.0 \times 10^{-2} M$ , (CAT) =  $2.0 \times 10^{-3} M$ ,  
 $[Ru(III)] = 2.4 \times 10^{-4} M$ , (Hypo) =  $4.0 \times 10^{-3} M$ ,  
 $\mu - 0.04 M$  (Maintained by NaClO<sub>4</sub>)

Time Minutes	$[HClO_4] = 1.2 \times 10^{-2} M$		$[HClO_4] = 1.6 \times 10^{-2} M$		$[HClO_4] = 2.0 \times 10^{-2} M$		$[HClO_4] = 3.0 \times 10^{-2} M$		$[HClO_4] = 4.0 \times 10^{-2} M$	
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	4.75		4.75		4.75		4.75		4.75	
10	4.35	4.25	4.25	4.25	4.0	4.0	3.75	3.75	4.0	3.8
20	4.2	4.05	4.05	4.05	3.85	3.85	3.7	3.7	3.5	3.6
30	4.0	3.85	3.85	3.85	3.65	3.65	3.5	3.5	3.25	3.3
40	3.8	3.65	3.65	3.65	3.35	3.35	3.2	3.2	2.9	3.05
60	3.45	3.35	3.35	3.35	2.8	2.8	2.6	2.6	2.3	2.65
90	3.05	2.8	2.8	2.8	2.5	2.5	2.25	2.25	1.95	1.95
120	2.8	2.5	2.5	2.5						1.65
150	2.4	2.25	2.25	2.25						1.25
	$k_{obs} \times 10^4$ (Sec <sup>-1</sup> )	0.48	0.60	0.60	0.88	0.88	1.10	1.10	1.33	1.33

(Obtained from Plots)

**Table-IV F-3: Effect in Variation of [Perchloric Acid] on the Rate of Oxidation of Diethanolamine at 35°C**  
 $(S) = 2.0 \times 10^{-2} M$ , (CAT) =  $2.0 \times 10^{-3} M$ ,  
 $[Ru(III)] = 2.4 \times 10^{-4} M$ , (Hypo) =  $4.0 \times 10^{-3} M$ ,  
 $\mu - 0.04 M$  (Maintained by NaClO<sub>4</sub>)

Time Minutes	$[HClO_4] = 1.2 \times 10^{-2} M$		$[HClO_4] = 1.6 \times 10^{-2} M$		$[HClO_4] = 2.0 \times 10^{-2} M$		$[HClO_4] = 3.0 \times 10^{-2} M$		$[HClO_4] = 4.0 \times 10^{-2} M$	
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	4.6		4.6		4.4		4.6		4.6	
5	4.4		4.3		4.25		4.1		3.9	
15	4.25		4.1		3.9		3.7		3.5	
25	4.1		3.9		3.65		3.3		3.05	
45	3.8		3.5		3.25		2.7		2.5	
60	3.5		3.2		2.75		2.4		2.05	
90	3.05		2.8		2.2		1.8		1.5	
120	2.7		2.4		1.8		1.35		1.0	
150	2.35		2.0		1.5		-		-	
$K_{obs} \times 10^4 \text{ (Sec}^{-1}\text{)}$		0.70	0.95		1.20		1.53		1.72	

(179)

(Obtained from Plots)

Table-IV F-4 : Effect is Variation of [Perchloric Acid] on the Rate of Oxidation of Triethanolamine at 35°C  
 $(S) = 2.0 \times 10^{-2} M$ , (CAT) =  $2.0 \times 10^{-3} M$ ,  
 $[Ru(III)] = 4.8 \times 10^{-4} M$ , (Hypo) =  $4.0 \times 10^{-3} M$ ,  
 $\mu - 0.04 M$  (Maintained by NaClO<sub>4</sub>)

Time Minutes	$\frac{[\text{HClO}_4]}{[\text{HClO}_4]} = 1.2 \times 10^{-2} \text{M}$	$\frac{[\text{HClO}_4]}{[\text{HClO}_4]} = 1.6 \times 10^{-2} \text{M}$	$\frac{[\text{HClO}_4]}{[\text{HClO}_4]} = 2.0 \times 10^{-2} \text{M}$	$[\text{HClO}_4] = 3.0 \times 10^{-2} \text{M}$	$[\text{HClO}_4] = 4.0 \times 10^{-2} \text{M}$
	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.	Vol. of Hypo used ml.
0	5.3	5.3	5.1	5.3	5.2
5	5.1	4.9	4.5	4.4	4.1
15	4.8	4.6	4.1	4.0	3.8
25	4.3	4.1	3.7	3.4	3.0
45	3.9	3.7	3.1	2.8	2.65
60	3.4	3.1	2.7	2.3	1.95
90	3.0	2.6	2.2	1.7	1.45
120	2.5	2.2	1.65	1.35	-
150	1.8	1.65	1.25	-	-
$k_{\text{obs}} \times 10^4 \text{ (Sec}^{-1}\text{)}$	0.76	1.10	1.50	1.72	1.91

(Obtained from Plots)

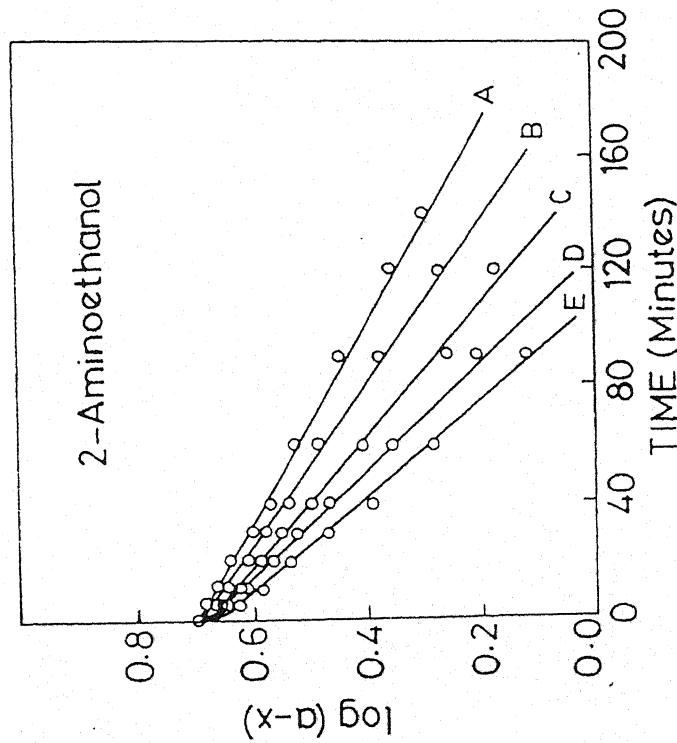
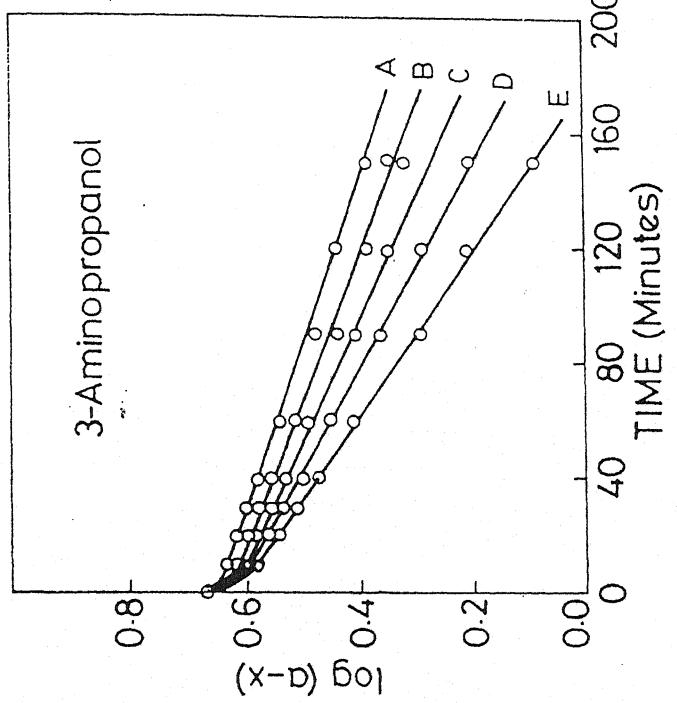


Fig. IV F-1 First order rate plots at 35°C  
 $[S] = 2.0 \times 10^{-2} \text{M}$ ,  $[\text{CAT}] = 2.0 \times 10^{-3} \text{M}$ ,  
 $[\text{Ru(III)}] = 4.8 \times 10^{-4} \text{M}$ ,  $(\text{HClO}_4) = 1.2, 1.6,$   
 $2.0, 3.0$  and  $4.0 \times 10^{-2} \text{M}$  for A, B, C, D and  
E respectively

Fig. IV F-2 First order rate plots at 35°C  
 $[S] = 2.0 \times 10^{-2} \text{M}$ ,  $[\text{CAT}] = 2.0 \times 10^{-3} \text{M}$ ,  
 $[\text{Ru(III)}] = 4.8 \times 10^{-4} \text{M}$ ,  $(\text{HClO}_4) = 1.2, 1.6,$   
 $2.0, 3.0$  and  $4.0 \times 10^{-2} \text{M}$  for A, B, C, D and  
E respectively

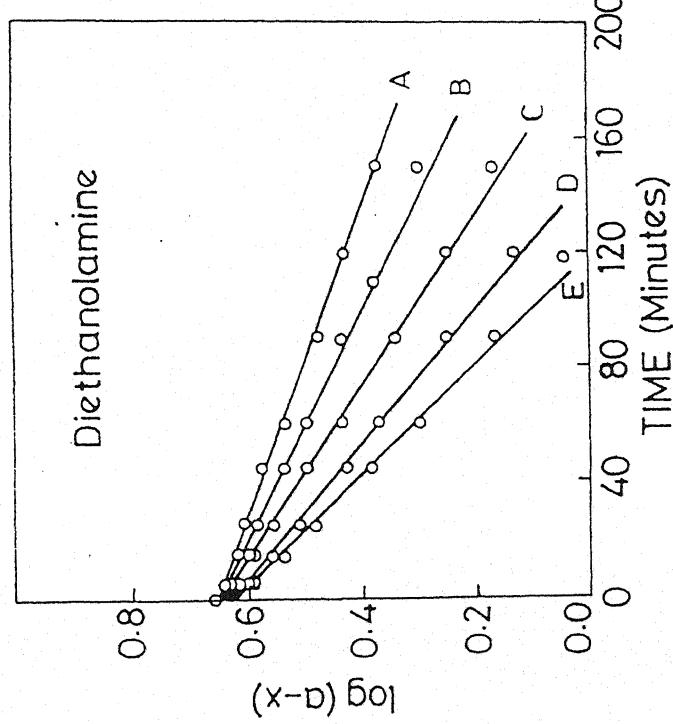


Fig. IV F-3 First order rate plots at 35°C  
 $[S] = 2.0 \times 10^{-2} M$   $[CAT] = 2.0 \times 10^{-3} M$ ,  
 $[Ru(III)] = 2.4 \times 10^{-4} M$ ,  $(HClO_4) = 1.2, 1.6,$   
 $2.0, 3.0$  and  $4.0 \times 10^{-2} M$  for A, B, C, D and  
E respectively

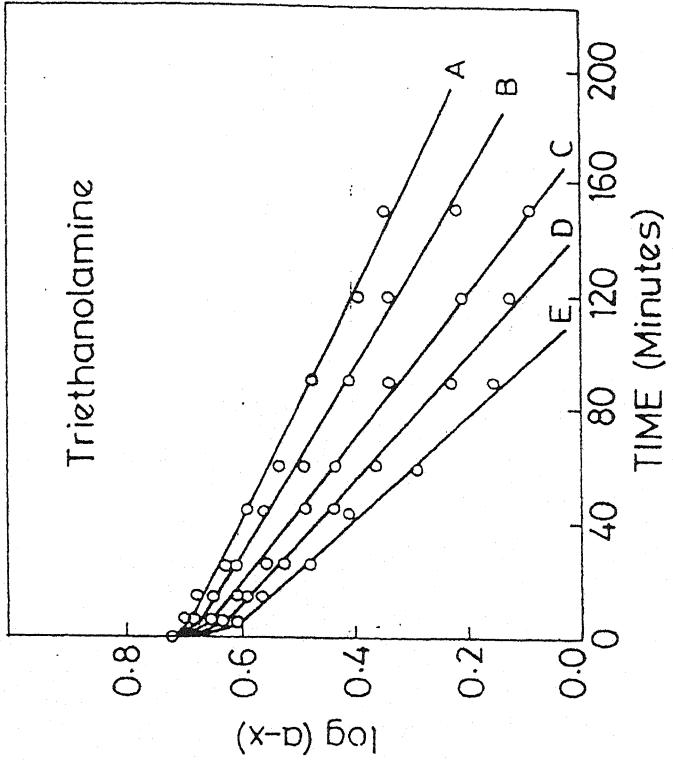


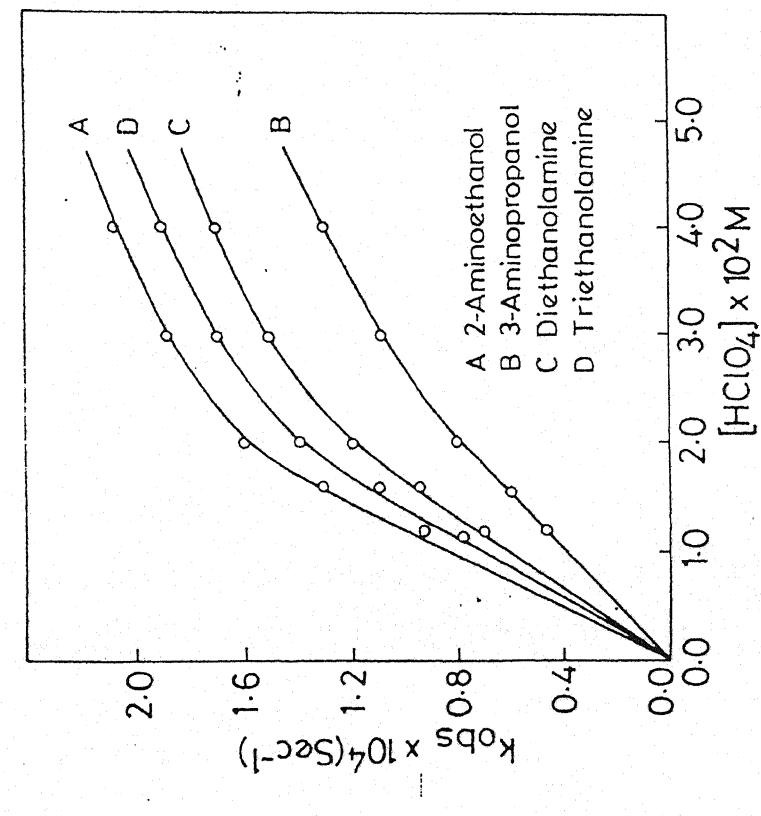
Fig. IV F-4 First order rate plots at 35°C  
 $[S] = 2.0 \times 10^{-2} M$   $[CAT] = 2.0 \times 10^{-3} M,$   
 $[Ru(III)] = 2.4 \times 10^{-4} M$ ,  $(HClO_4) = 1.2, 1.6,$   
 $2.0, 3.0$  and  $4.0 \times 10^{-2} M$  for A, B, C, D and  
E respectively

**Table-IV F-5 : Effect of [Perchloric Acid] on the Rate Constants at 35°C**

[Perchloric Acid] 10 <sup>2</sup> M	2 - Aminoethanol	3 - Aminopropanol	Diethanolamine	Triethanolamine	$k_{obs.} \times 10^4 \text{ sec}^{-1}$
1.2	0.96	0.48	0.70	0.76	
1.6	1.33	0.60	0.95		1.10
2.0	1.60	0.88	1.20		1.50
3.0	1.91	1.10	1.53		1.72
4.0	2.12	1.33	1.72		1.91

(183)

Sodium meta periodate; [Aminoalcohol] = 2.0 × 10<sup>-2</sup>M and [RuCl<sub>3</sub>] = 2.4 × 10<sup>-4</sup>M and 4.8 × 10<sup>-4</sup>M for 2 - Aminoethanol,  $\mu = 0.04\text{M}$  maintained by NaClO<sub>4</sub>..



(184)

Fig.IV F-5 Plot of  $K_{obs}$  versus  $(\text{HClO}_4)$  at  $35^\circ\text{C}$   
 $[\text{Aminoalcohol}] = 2.0 \times 10^{-2}\text{M}$ ,  $[\text{CAT}] = 2.0 \times 10^{-3}\text{M}$ ,  
 $[\text{Ru(III)}] = 4.8 \times 10^{-4}\text{M}$  for A and  $2.4 \times 10^{-4}\text{M}$  for B,  
C and D.

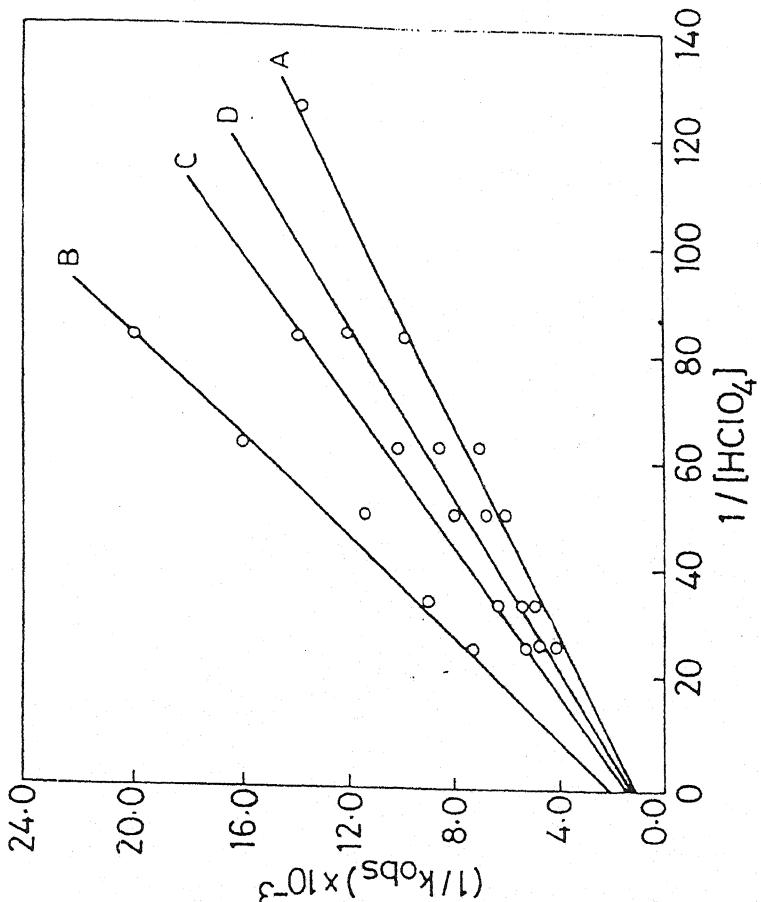


Fig.IV F-6 Plot of  $1/K_{obs}$  versus  $(\text{HClO}_4)$  at  $35^\circ\text{C}$   
 $[\text{Aminoalcohol}] = 2.0 \times 10^{-2}\text{M}$ ,  $[\text{CAT}] = 2.0 \times 10^{-3}\text{M}$ ,  
 $[\text{Ru(III)}] = 4.8 \times 10^{-4}\text{M}$  for B, C and D.

aminoalcohols may be summarised as in Table IV F-5 the table shows that an increase in coencentration of perchloric acid increases the observed rate constant. The Plot of  $k_{\text{obs.}}$  versus  $(\text{HClO}_4)$  showed a deviation from linearly (Figure IV F-5), while the plots of  $1/k_{\text{obs.}}$  versus  $1/(\text{HClO}_4)$  were linear with intercepts (Figure IV F-6). It, therefore, appears that order of reaction in acid decreases from unity to zero at higher acid concentrations.

## **IV G    Influence of neutral salt**

The effect of addition of neutral salt viz., sodium meta periodate was studied on the rate of oxidation in each case. The concentrations of aminoalcohol, Sodium meta periodate perchloric acid and ruthenium (III) were kept constant at  $2.0 \times 10^{-2}\text{M}$ ,  $2.0 \times 10^{-3}\text{M}$ ,  $2.0 \times 10^{-2}\text{M}$  ( $4.8 \times 10^{-4}\text{M}$  in case of 2–aminoethanol) respectively. The values of observed rate constants for the oxidation of various aminoalcohols are summarised in Table IV G-1. It is predicted from the table that the addition of salt has a slight positive effect on the rate of reaction.

## **IV H    Effect of $\text{Cl}^-$ on the rate of reaction**

In order to a certain the effect of  $\text{Cl}^-$  ion on the rate of reaction, the reactions have investigated at several initial concentrations of sodiumchloride keeping sodium meta periodate, aminoalcohol ( $2.0 \times 10^{-2}\text{M}$ ),  $\text{HClO}_4$  ( $2.0 \times 10^{-2}\text{M}$ ) and ruthenium (III)  $2.4 \times 10^{-4}\text{M}$  ( $4.8 \times 10^{-4}\text{M}$  in case of 2–aminoethanol) constants. The results of

**Table-IV G-1: Effect of [Sodium Perchlorate] on the Rate Constants at 35°C**

[Sodium Perchlorate] 10 <sup>3</sup> M	k <sub>obs.</sub> × 10 <sup>4</sup> sec <sup>-1</sup>	2-Aminoethanol	3-Aminopropanol	Diethanolamine	Triethanolamine
5.0	1.54	1.15	1.72	1.15	
10.0	1.75	1.33	1.91	1.20	
15.0	1.91	1.80	2.12	1.33	
20.0	2.30	2.12	2.30	1.72	

Sodium meta periodate; [Aminoalcohol] = 2.0 × 10<sup>-2</sup>M, [HClO<sub>4</sub>] = 2.0 × 10<sup>-2</sup>M, [Ru(III)] = 2.4 × 10<sup>-4</sup>M, (4.8 × 10<sup>-4</sup>M in case of 2-aminoethanol).

**Table-IV H-1: Effect of [Sodium Chloride] on the Rate Constants at 35°C**

[Sodium Chlorate] $10^2$ M	$k_{\text{obs.}} \times 10^4 \text{ sec}^{-1}$	
	Diethanolamine	Triethanolamine
0.5	1.20	1.15
1.0	1.40	1.25
1.5	1.60	1.50
2.0	1.91	1.80

Sodium meta periodate.;  $[\text{HClO}_4] = 2.0 \times 10^{-2}$ M,  $[\text{RuCl}_3] = 2.4 \times 10^{-4}$ M and [Aminoalcohol] =  $2.0 \times 10^{-2}$ M,

effect of NaCl in case of diethanolamine and triethanolamine are presented in Table-IV H-1. It is clear from the table that an addition of sodium chloride in the reaction mixture increases the rate constant.

## **IV I      Effect of variation in temperature**

To investigate the effect of variation in temperature, the reactions were carried out at four different temperature viz., 35, 40, 45 and 50°C. The reactants concentrations have been kept constant as  $2.0 \times 10^{-3}$ M Sodium meta periodate,  $2.0 \times 10^{-2}$ M aminoalcohol,  $2.0 \times 10^{-2}$ M,  $\text{HClO}_4$  and  $2.4 \times 10^{-4}$ M ruthenium (III) [in case of 2–aminoethanol  $4.8 \times 10^{-4}$ M ruthenium (III)]. The values of observed rate constants are presented in Table -IV I-1. The values of energy of activation evaluated from the slopes of the straight lines plotted between  $\log k_{\text{obs}}$  versus reciprocal of absolute temperature ( $1/T$ ) \*Figure -IV I-1) were as  $57.5 \pm 0.5$ ,  $48.8 \pm 0.5$ ,  $29.9 \pm 0.5$  and  $25.5 \pm 0.5$   $\text{kJmol}^{-1}$  for the oxidation of 2–aminoethanol, 3–aminopropanol, diethanolamine and triethanolamine respectively.

**Table-IV I-1 : Effect of temperature on the Rate Constants**

Temperature (°C)	$k_{obs.} \times 10^4 \text{ sec}^{-1}$		
	2-Aminoethanol	3-Aminopropanol	Diethanolamine
35	1.60	0.88	1.20
40	2.30	1.27	1.43
45	3.06	1.52	1.72
50	-	1.90	1.92
			2.30

(189)

[Sodium meta periodate] =  $2.0 \times 10^3 \text{M}$ ; [Aminoalcohol] =  $2.0 \times 10^{-2} \text{M}$ ,  $[\text{HClO}_4] = 2.0 \times 10^{-2} \text{M}$   $[\text{RuCl}_3] = 2.4 \times 10^{-4} \text{M}$  for 3-aminopropanol, Diethanolamine, Triethanolamine and  $4.8 \times 10^{-4} \text{M}$  for 2-aminoethanol).

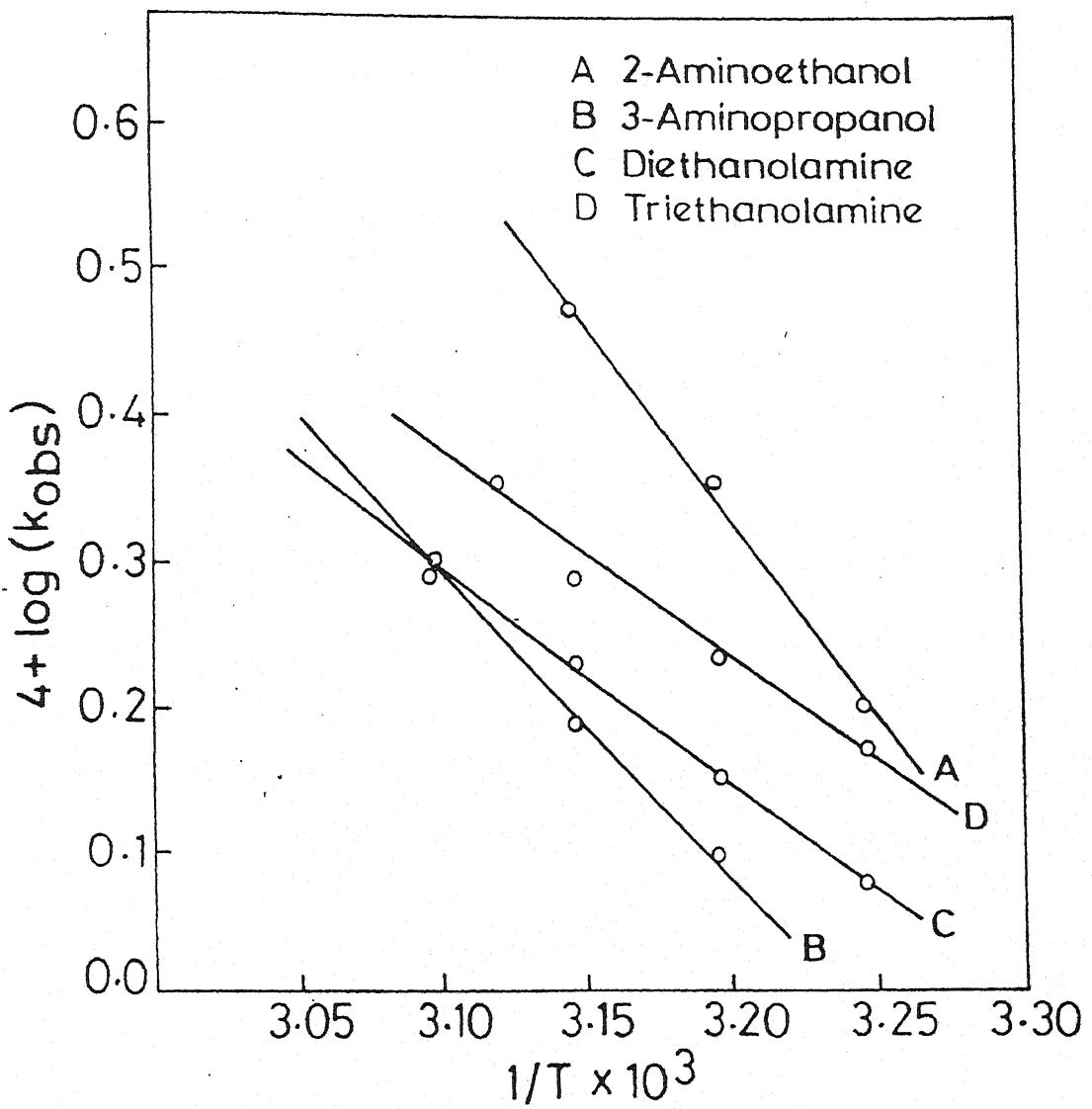


Fig. IV I-1 Arrhenius plot of  $\log (k_{\text{obs}})$  vs  $(1/T)$

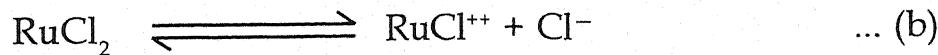
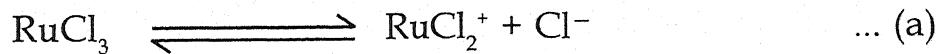
$[\text{CAT}] = 2.0 \times 10^{-3} \text{M}$ ,  $[\text{S}] = 2.0 \times 10^{-2} \text{M}$

$[\text{HClO}_4] = 2.0 \times 10^{-2} \text{M}$ ,  $[\text{Ru(III)}] = 2.4 \times 10^{-4} \text{M}$  for B, C and D  
 $4.8 \times 10^{-4} \text{ M}$  for A.

## Discussion

The oxidation of primary (2-aminoethanol, 3-aminopropanol) secondary (diethanolamine) and tertiary (triethanolamine), aminoalcohols followed almost similar kinetics. The order of reaction in each sodium meta periodate and catalyst is unity, which that in substrate is zero. The order in acid is unity at lower acid concentrations and decreases from unity, at higher acid concentrations.

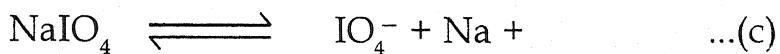
In dilute hydrochloric acid solution the ruthenium tri chloride exists<sup>16</sup> as  $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{RuCl}(\text{H}_2\text{O})_5]^{2+}$  and  $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$ . These species can be separated by ion exchange and identified by their electronic spectra. The existence of  $\text{RuCl}_3$ ,  $\text{RuCl}_2^+$  and  $\text{RuCl}^{++}$  in dilute HCl solution of  $\text{RuCl}_3$  has also been shown by Connick and Fine<sup>17</sup>. The following equilibrium may be considered between these species:



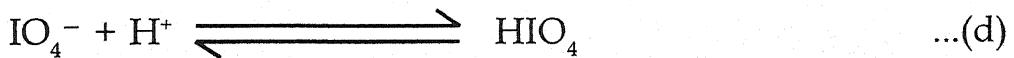
Thus acting species of the catalyst will depend upon the effect of  $\text{Cl}^-$ . A positive effect of  $\text{Cl}^-$  on the rate of reaction clearly suggests that the neutral species i.e.  $\text{RuCl}_3$  is the reacting species of the catalyst

in the present case. The mechanism for the oxidation of diols<sup>18</sup> by sodium meta periodate in presence of ruthenium (III) chloride as catalyst in HCl (0.01 – 0.80 M) has also been proposed by considering the neutral form of the catalyst i.e. RuCl<sub>3</sub> as the reacting species of the catalyst.

Sodium meta periodate behaves like a strong electrolyte and in aqueous solutions, ionises as,



The protonation of Sodium meta periodate has been thoroughly investigated<sup>19</sup>. The anion gets protonated in acid solution to give periodic acid as follows,

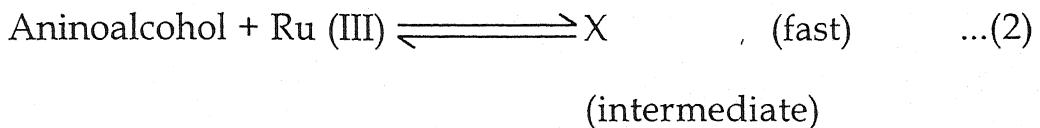
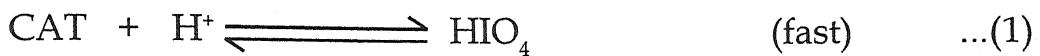


$$K = 3.8 \times 10^4 \text{ at } 25^\circ\text{C}$$

Studies on ruthenium (III) catalysed oxidation of aminoalcohols by other oxidant viz., hexacyanoferrate (III)<sup>10,11</sup> in alkaline medium and cerium (IV)<sup>12</sup> in acidic medium have shown that the ruthenium (III) catalysed oxidation of aminoalcohols proceed via an intermediate complex formation between the substrate and the reacting species of the catalyst.

On the basis of these facts and experimental results, the mechanism for the ruthenium (III) catalysed oxidation of aminoalcohols by Sodium meta periodate may be proposed as

follows,



The rate of disappearance of Sodium meta periodate may be given as,

$$-\frac{d[\text{CAT}]}{dt} = K_3 [X] [\text{HIO}_4] \quad \dots(4)$$

Again the total concentration of sodium meta periodate and catalyst are given by equations (5) and (6), respectively.

$$[\text{CAT}]_T = [\text{CAT}] + [\text{HIO}_4] \quad \dots(5)$$

and

$$[\text{Ru(III)}]_T = [\text{Ru (III)}] + [X] \quad \dots(6)$$

also

$$[\text{HIO}_4] = K_1 [\text{CAT}] [\text{H}^+] \quad \text{from step (1)} \quad \dots(7)$$

and

$$[X] = K_2 [\text{RU(III)}] [\text{Aminoalcohol}] \quad \text{from step (2)} \quad \dots(8)$$

Thus finding  $[\text{HIO}_4]$  and  $[\text{X}]$ , in terms of  $[\text{CAT}]_T$  and  $[\text{Ru(III)}]_T$  respectively and substituting in equation (4), the rate law equation converted to the euqation (9).

$$\frac{-d(\text{CAT})}{dt} = \frac{K_3 K_1 K_2 (H^+) (\text{Aminoalcohol}) (\text{CAT})_T [\text{Ru(III)}]_T}{\{1 + K_1 (H^+)\} \{1 + K_2 (\text{Aminoalcohol})\}} \dots (9)$$

Since step (2), is very fast and rate of oxidation is independent of [aminoalcohol], it is likely that  $K_2 [\text{Aminoalcohol}] \gg 1$  and, therefore, the rate law equation (9), takes the form,

$$\frac{-d(\text{CAT})}{dt} = \frac{K_3 K_1 (H^+) (\text{CAT})_T [\text{Ru(III)}]_T}{\{1 + K_1 (H^+)\}} \dots (10)$$

According to rate law equation (10), the order of reaction in oxidant and catalyst is unity which has also been observed experimentally. Further, a plot of  $1/(\text{rate constant})$  versus  $1/[H^+]$  should be linear with intercept. The value of equilibrium constant ( $K_1$ ) obtained from the intercept and slope of such a plot is independent of aminoalcohol. The equilibrium constant ( $K_1$ ) obtained from the slope and intercept of the double reciprocal plots (Figure IV F-6), were 15.0 13.5, 16.4 and 16.6 for 2-aminoethanol, 3-aminopropanol, diethanolamine and triethanolamine respectively i.e. nearly identical within the experimental error.

The value of  $K = 3.8 \times 10^4$  at  $25^\circ\text{C}$  equation (d) : for protonation of Sodium meta periodate was obtained<sup>19,20</sup> from the activity ionisation constant data. During the ionisation constant measurement, the suitable mathematical equations were developed to overcome

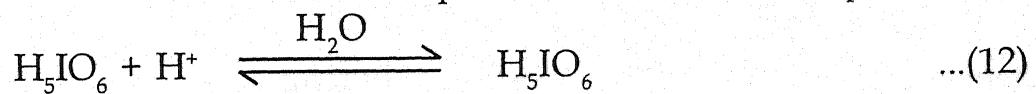
complications caused by simultaneous occurrence of other equilibrium processes (disproportionation and/or hydrolysis of periodic acid) along with the ionisation equilibrium. It is also mentioned that the values calculated for the period before beginning of precipitation of periodate are less reliable because of the greater errors involved in the measurement of the small amounts of added acid. A very small amount basic impurities in Sodium meta periodate had a much more pronounced effect on the  $K$  values. In the present studies the experimental conditions are different ( $35^{\circ}\text{C}$ , acid effect has been studied at constant ionic strength). The other equilibria i.e. disproportionation or hydrolysis of periodic acid has not been considered. These factors may be responsible for the difference in the value of  $K_1$  (derived from kinetics) and  $K$  value shown in equation (d).

Further, at higher Acid concentrations where  $K_1[\text{H}^+] \gg 1$ , the rate law equation (10) reduces to,

$$-\frac{d[\text{CAT}]}{dt} = K_3[\text{CAT}]_T[\text{Ru(III)}]_T \quad \dots(11)$$

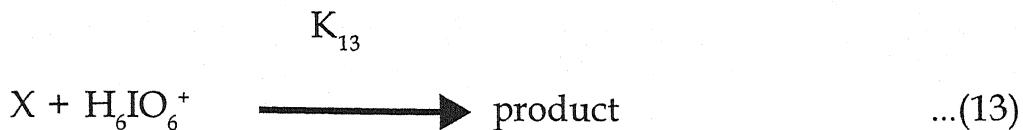
The experimental results are in agreement with the rate law equation (10) and (11).

The mechanism may also be proposed by considering further, protonation of periodic acid. The protonation of periodic acid in acidic solution of sodium meta periodate has also been reported<sup>21-25</sup> as,



$$(K_{12} = 1.02 \times 10^2 \text{ at } 25^{\circ}\text{C})$$

Thus by assuming that in acidic medium sodium meta periodate exists as  $\text{H}_5\text{IO}_6^+$  and by considering its further, protonation as equation (12), the step (3) of the proposed mechanism may be replaced by step (13) as,



Now the total concentration of Sodium meta periodate may be given as,

$$\text{CAT}_T = [\text{H}_5\text{IO}_6] + \text{I}(\text{OH})_6^+ \quad \dots(14)$$

and the corresponding rate law equation may be obtained as,

$$\frac{-d(\text{CAT})}{dt} = \frac{K_{13} K_2 K_{12} (\text{H}^+) (\text{CAT})_T [\text{Ru(III)}]_T (\text{Aminoalcohol})}{\{1 + K_{12} (\text{H}^+)\} \{1 + K_2 (\text{Aminoalcohol})\}} \quad \dots(15)$$

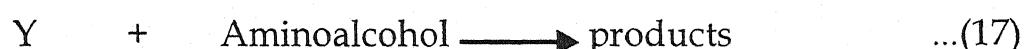
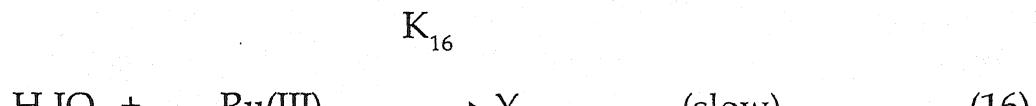
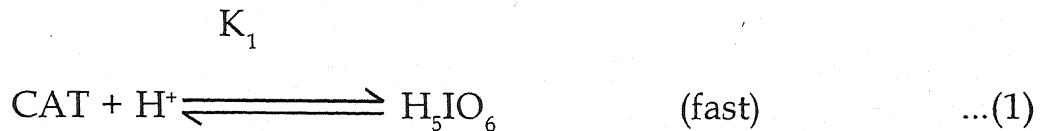
which is similar as rate law equation (9). However, the value of equilibrium constant  $K_{12}$  obtained from the double reciprocal plots (Figure IV F-6) is more close to the reported value of equilibrium constant (equation 12).

A slight positive salt effect can also be explained on the basis of involvement of similarly charged species in rate determining step (13).

Thus the kinetics results are well explained by considering  $[\text{H}_5\text{IO}_6^+]$  or  $\text{I}(\text{OH})_6^+$  as the reacting species of sodium meta periodate.

Ruthenium (III) catalysed oxidation of diols<sup>18</sup> by sodium meta periodate in acidic medium has been shown to proceed via a

intermediate adduct, between  $\text{RuCl}_3$  and protonasted species of the oxidant. Formation of a Cyclic complex between  $\text{RNHCl}$  and the catalyst  $\text{OSO}_4$  has also been proposed by Mushran et al.<sup>26,27</sup> By considering an adduct between  $\text{RuCl}_3$  and sodium meta periodate, the mechanism for the oxidation of aminoalcohols may be proposed as,



and the corresponding rate law equation may be obtained as,

$$\frac{-d(\text{CAT})}{dt} = \frac{K_{16} K_1 (\text{CAT})_T (\text{H}^+) [\text{Ru(III)}]}{\{1 + K_1 (\text{H}^+)\}} \quad \dots(18)$$

It is evident from rate law equation (18), that for the double reciprocal plot (Figure IV F- 6) both intercept and slop should be independent of the aminoalcohol. However figure IV F- 6 indicates that the intercepts and gradients for four different aminoalcohols are quite clearly at variance with one another. Therefore, the results are not consistent with the mechanism involving the adduct between sodium meta periodate and  $\text{RuCl}_3$ .

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## **Chapter - V**

### ***Conclusion***

# Conclusion

The oxidation of five reducing sugars viz. glucose, fructose, galactose, maltose and lactose by sodium metaperiodate in presence of  $\text{RuCl}_3$  have been studied (Chapter III). The kinetic result and proposed mechanism in presence of the catalyst are summarised as follows:

## 1. Effect of oxidant on the rate:

The order of reaction with respect of sodium metaperiodate was found to be unity during a particular kinetic run. However, the observed rate constant ( $k_{\text{obs}}$ ) was found to decrease with a increase in  $[\text{IO}_4^-]$ .

## 2. Effect of substrate on the rate:

The reaction was first order in substrate as lower concentrations. However, the order of reaction decreases from unity to zero at highter [substrate].

## 3. Effect of alkali on the rate:

The order of reaction with respect to alkali was found to be unity at lower  $[\text{OH}^-]$ . The order of reaction at higher  $[\text{OH}^-]$  decreases from unity to zero.

## 4. Effect of catalyst on the rate:

The plot of  $(k_{\text{obs}})$  versus  $[\text{RuCl}_3]$  (Figure III F-6) was linear with an intercept suggesting that rate is proportional to  $\{k' + k''[\text{RuCl}_3]\}$  where  $k'$  and  $k''$  are rate constant for uncatalysed and catalysed

path, respectively. The reactions were also studied in absence of the catalyst and were found to be extremely slow. The observed rate constant for uncatalysed path ( $k'$ ) i.e.  $k_{\text{obs}}$  at  $[\text{RuCl}_3] = 0$ , was matching with the value of intercept of the plot of ( $k_{\text{obs}}$ ) versus  $[\text{RuCl}_3]$  in case of each reducing sugar.

## 5. Ionic effect

Negligible effect of ionic strength was observed.

## 6. Oxidation products

*kinetic conditions*

Under the experimental conditions of the kinetic the reducing sugar oxidised to formaldehyde and corresponding lower aldonic acid. Under the stoichiometric conditions the formaldehyde is further oxidised in presence of excess of the oxidant.

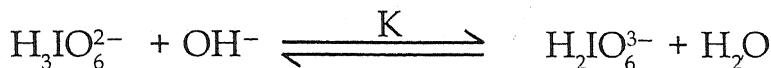
## 7- Activation parameter:

	FR (A)	GL (B)	GA (C)	MA (D)	LA (E)
$E_{\text{act}}$ (kJ mol <sup>-1</sup> )	58.80 $\pm 0.50$	76.50 $\pm 0.50$	63.79 $\pm 0.50$	69.59 $\pm 0.50$	85.05 $\pm 0.50$
$\log A$	6.58	9.35	7.35	8.30	10.75
$\Delta H^{\#}$ (kJ mol <sup>-1</sup> )	56.17 $\pm 0.50$	73.87 $\pm 0.50$	61.17 $\pm 0.50$	66.96 $\pm 0.50$	82.45 $\pm 0.50$
$\Delta S^{\#}$ (JK <sup>-1</sup> mol <sup>-1</sup> )	-119.17 $\pm 1.0$	-66.09 $\pm 0.50$	-104.44 $\pm 0.50$	-86.22 $\pm 1.0$	-39.54 $\pm 0.50$
$\Delta G^{\#}$ (kJ mol <sup>-1</sup> )	93.77 $\pm 1.0$	94.72 $\pm 1.0$	94.22 $\pm 1.0$	94.16 $\pm 1.0$	94.87 $\pm 1.0$

## 8- Reactive species:

### (a) Oxidant

In the pH range employed in the present investigations, the reactive species of the oxidant are expected to be  $(H_3IO_6^{2-})$  and  $(H_2IO_6^{3-})$  with the following equilibrium



### (b) Substrate

In present investigations, the enediol anion of the sugar has been considered as the reacting species of reducing sugar.

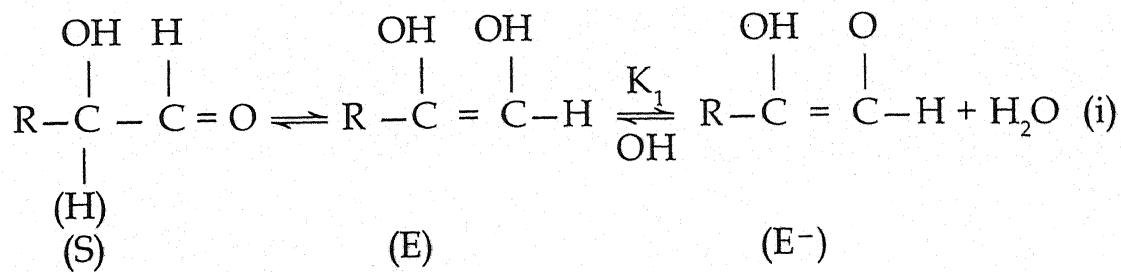
### (c) Catalyst

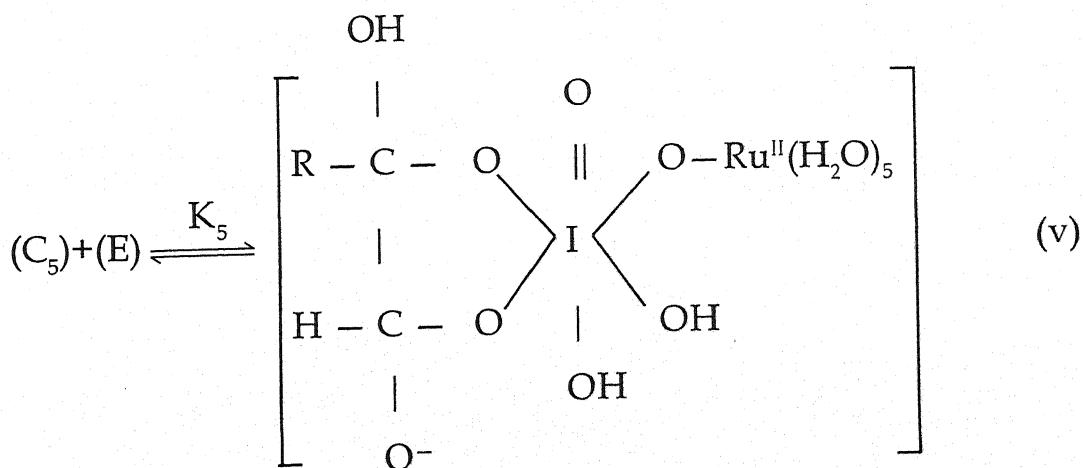
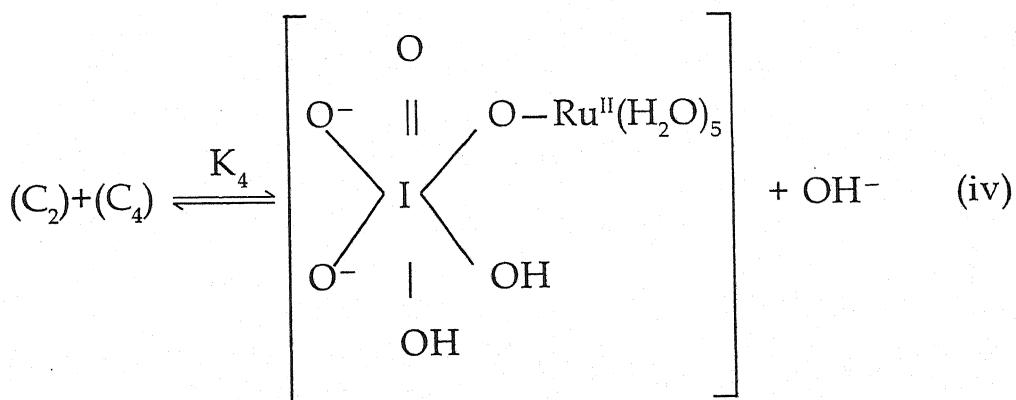
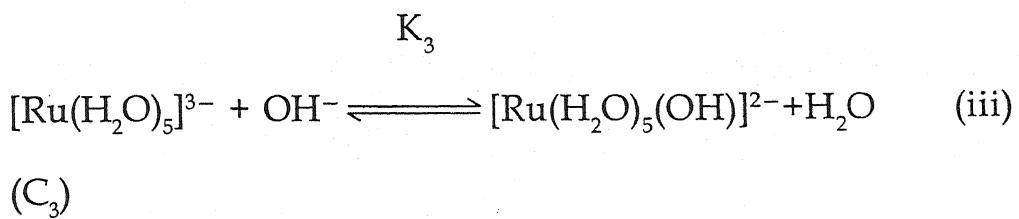
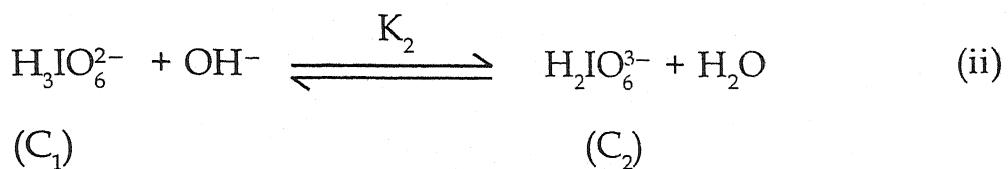
The species  $[Ru(H_2O)_5(OH^-)]^{2+}$  has been observed as the reactive species of the catalyst.

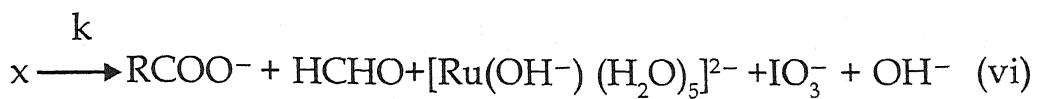
## 9. Complex formation studies

The formation of the  $\{Ru^{III} - IO_4^-\}$  complex has been confirmed by spectrophotometric evidence.

## 10. Proposed mechanistic steps:







## 11. Derived rate law on the basis of proposed mechanism:

The rate law which explains all the experimental results in presence of ruthenium (III) has been derived as follows:

$$\frac{-d[\text{IO}_4^-]}{dt} = \frac{kK'[\text{OH}^-][\text{S}][\text{CAT}]_T[\text{IO}_4^-]_T}{(K_2 + K_3) + K_2K_3[\text{OH}^-] + K'[\text{OH}^-][\text{S}][\text{IO}_4^-]_T}$$

The rate law also indicate that the order of reaction with respect to catalyst is always unity. On the basis of the above results and mechanism it may be concluded that retuenium (III) works as the catalyst in above reactions.

The oxidation of four amino alcohols viz. 2–amino ethanol, 3–amino proponol, diethanolamine and triethanolamine by sodium meta periodate in presence of ruthenium (III) catalyst in acidic medium have also been studied (Chapter IV).

The kinetic results and proposed mechanism in presence of the  $\text{RuCl}_3$  are summarised as follows:

## **1. Effect of variation in sodium metaperiodate concentration**

The kinetic results suggest that observed rate constants remained nearly identical at various initial concentration of  $[\text{IO}_4^-]$  in case of each amino alcohol, which further confirmed first order dependence of rate with respect to  $[\text{IO}_4^-]$ .

## **2. Effect of variation in ruthenium (III) concentration**

The results of the effect of ruthenium (III) concentration suggest that an increase in  $\text{RuCl}_3$  concentration proportionally increases the observed psuedo first rate constant with respect to  $[\text{IO}_4^-]$ .

The plots of  $(K_{\text{obs}})$  versus  $\text{RuCl}_3$  figure (IV E–5) represent straight lines passing through origin. The reaction is, therefore, of first order with respect to  $\text{RuCl}_3$  concentration.

### **3. Effect of variation in amino alcohol concentrations:**

The results suggest that an increase in the initial concentration of amino alcohols resulted in a negligible effect on the rate constants. It therefore appears that the order of reaction in amino alcohol is zero.

### **4. Effect of variation in perchloric acid concentrations**

The plots of ( $k_{\text{obs}}$ ) versus ( $\text{HClO}_4$ ) figure IV F-5 showed a deviation from linearity while that plots of  $1/(k_{\text{obs}})$  versus  $1/[\text{HClO}_4]$  figure IV F-6, were linear with intercepts. It therefore suggests that order of reaction in acid decreases from unity to zero at higher acid concentrations.

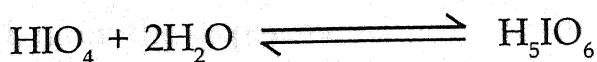
### **5. Effect of $\text{Cl}^-$ on the rate of reaction**

The results of effect of  $\text{NaCl}$  table IV H-1 show that on addition of sodium chloride in the reaction mixture increases the rate of reaction.

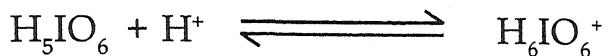
### **6. Reactive species.**

#### **(i) Oxidant**

In the pH range employed in the present investigations, the reactive species of the oxidant are expected to be  $\text{H}_6\text{IO}_6^+$  or  $[\text{I}(\text{OH})_6]^+$ .



K



## (ii) Substrate

In the present investigations primary, secondary and tertiary amino alcohols have been considered as the reacting species.

## (iii) Catalyst

A positive effect of  $\text{Cl}^-$  on the rate of reaction has been observed in the present investigation.

This suggests that the neutral species i.e.  $\text{RuCl}_3$  is the reacting species of the catalyst.

## 7. Effect of variation in temperature

In the present investigation the reaction were carried out at a for different temperature viz. 35, 40, 45 and 50°C. The reactant concentration as have been kept constant table IV-I-1 and Figure IV-I-1. The values of energy of activation were as  $57.5 \pm 0.5$ ,  $48.8 \pm 0.5$ ,  $29.9 \pm 0.5$  and  $25.5 \pm 0.5 \text{ kJ mol}^{-1}$  for the oxidation of 2 – amino ethanol, 3 – amino propanol diethanolamine and triethanolamine respectively.

## 8. Oxidation products

### *kinetic conditions*

Under the experimental conditions of the kinetic, the amino

alcohols oxidised to formaldehyde and corresponding carboxylic acids.

On the basis of these findings and the proposed mechanism the rate law which explains all the experimental results in presence of ruthnium (III) has been derived as follows-

$$\frac{-d(CAT)}{dt} = \frac{K_{16} K_1 (CAT)_T (H^+) [Ru(III)]}{\{1 + K_1 (H^+)\}} \quad \dots(18)$$

It is evident from rate law equation (18), that for the double reciprocal plot (Figure IV F - 6) both intercept and slop should be independent of the aminoalcohol. However figure (IV F - 6) indicates that the intercepts and gradients for four different aminoalcohols are quite clearly at variance with one another. Therefore, the results are not consistent with the mechanism involving the adduct between sodium meta periodate and  $RuCl_3$ .